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Review

Blocked isocyanates III

Part B: Uses and applications of blocked isocyanates

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Abstract

As the completion of the third installment in the series of reviews of the literature on blocked isocyanates, Parts A and B of this review bring together the most important developments documented in over 1700 patents and publications that have been printed between 1980 and mid-2000. For references before 1980, see earlier reviews in this series [Prog. Org. Coat. 3 (1975) 73; Prog. Org. Coat. 9 (1981) 3]. The uses and applications of blocked isocyanates in coatings and non-coatings fields are reviewed. Part A: *Mechanisms and Chemistry* was published earlier in this journal [Prog. Org. Coat. 36 (1999) 148]. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Blocked isocyanate; Coil; Powder; Waterborne; Automotive; E-coat; Wire; Coatings; Adhesives; Sealants; Plastics; Rubber; Textile; Paper; Electronics; Photographic; Printing; Copying applications

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Introduction

The most impressive point of note for the progress since the beginning of this review series is the expansion of industrial uses for blocked isocyanates. The patent literature reviewed here demonstrates that blocked isocyanates have been investigated for almost every type of coatings application and for a diverse number of non-coatings uses. Within the market, blocked isocyanates have wide spread use in many coatings areas: automotive, maintenance, and industrial finishing.

This paper is a continuation of Part A of a blocked isocyanate review published earlier that covered kinetics, mechanisms, catalysts, and blocking groups [1]. The sections are numbered continuing the numbering of the first paper to facilitate cross-referencing. Cross-references to sections in Sections 1–3, that do not specify that they are in the addendum to this paper are found in Part A. However, reference numbering is independent of Part A, several references are repeated in this part with new numbers. In general, we have only included in the text the blocked isocyanate and coreactant(s) not the other binders that might be incorporated in a formulation, the additives, pigments, and so forth. We have usually only given one of several examples covered in a patent. No attempt was made to rank the patents in terms of commercial importance. We have not included the many patents that state that blocked isocyanates can be used as alternative cross-linkers but do not give any examples showing such a use.

The literature for this paper was searched from 1980 through mid-2000. For reference before 1980 see earlier reviews in this series [2]. During the writing of this second part of the paper, it became very obvious that our initial search had greatly underestimated the extent of the literature. Through cross-referencing and additional searches based on authors, we found many more significant contributions that were not picked up by electronically searching for “blocked isocyanates” or “blocked polyisocyanates”. We will not venture to guess the extent of what was missed in the first pass (or indeed in what we have done since then). We have included about 700 references that were not found in our first pass.

In an addendum at the end of the paper are additions to some sections of Part A found since it was submitted. These additions cover new literature published in the last year, as well as ones found using our new searches. There are some corrections to Part A included in the addendum. Appendix A gives the acronyms we are using and Appendix B gives the trade names and compositions of blocked isocyanates available in the open literature that are or have been commercially available.

4. Waterborne systems

Since waterborne coatings are used in many different applications, we have made this separate section to bring together the different approaches to their use. We have included here only examples of each of the many ways in which blocked isocyanates are used; many more applications are shown in the various end use sections. E-coat usage is not described here but in Section 5.3.

One of the major advantages of blocked isocyanates is that they can be formulated into waterborne coatings with less concern for the isocyanate reacting with water. Most blocked isocyanates have sufficient stability to be used in one package (1K) waterborne coatings to cross-link polyols. We have found no systematic investigation of stability in the literature; several factors may be involved. Isocyanate structure can affect stability. One would expect aliphatic systems to be more stable than aromatic ones. It has been reported that the hydrolytic stability in the pH range of 7.5–9.0 of methyl ethyl ketone oxime (MEKO) blocked 2,4-toluene diisocyanate (TDI) is insufficient for the formulation of 1K coatings [3]. On the other hand, many aliphatic systems are adequately stable in the same system.

Phase separation of the blocked isocyanate from water may well be a factor in stability. If the blocked isocyanate is completely isolated in the organic phase, stability would be expected to be better because of reduced exposure to water. Emulsions of MEKO blocked 4,4'-diphenylmethane diisocyanate (MDI) are reported to be stable for 3 months at 20°C [4]. Blocking agent structure is probably another factor, if the deblocking temperature is higher as with alcohols, e.g., one would expect higher stability than with a low temperature deblocking agent such as MEKO. How-

ever, as discussed in Section 2.2.3, use of diethyl malonate (DEM) blocked TDI, a low cure temperature system, in waterborne coatings has been patented. Malonic ester blocked isocyanates do not react via splitting to isocyanate and malonic ester; perhaps this accounts for the high stability in the presence of water. However, the rate of hydrolysis of DEM blocked isocyanates has not been studied. On the other hand, it has been reported that the hydrolytic stability of ethyl acetoacetate blocked isocyanates that also undergo anomalous cross-linking reactions is too poor to permit their use in waterborne coatings [5].

Water solubility of the blocking agent may be a factor. At any temperature there will be an equilibrium between blocked isocyanate and isocyanate + blocking agent. If the blocking agent is water soluble, it would increase the probability of reaction of the isocyanate with the very large excess of water present, driving the reaction towards deblocking. With relatively high molecular weight polyether diols partially reacted with TDI and a blocking agent such as imidazole diluted with water give a dispersion that gels to a hydrogel in 40 min at 20°C. A similar material blocked with ϵ -caprolactam (CL) does not gel in 1 week. In contrast a control dispersion made without the blocking agent gelation occurs after only 2 min [6]. The imidazole blocked product has been used to make hydrogels for various purposes (see Section 13).

The pH may be a factor. Note that in [3] the author gives a pH range of stability (without giving experimental evidence). Even in E-coat, where very long residence times at mildly acidic or basic pH's are encountered, blocked isocyanates are used. The above suggestions are consistent with formulations for cationic E-coat primers where very long term resistance to reaction with water is required, aromatic isocyanates are used but the blocked isocyanate is present only in the dispersed organic aggregate phase. In early E-coat formulations, 2-ethylhexyl alcohol (2EH) was used. Not only does 2EH give a high deblocking temperature, it is also essentially insoluble in water. As will be discussed in Section 5.3, formulation refinements over time have made possible the use of lower temperature deblocking isocyanates including aliphatic isocyanates.

In the case of the most reactive systems, such as with amine coreactants, adequate pot life for two package (2K) coatings is usually achievable. Additionally, if the blocked isocyanate is not storage stable in water, it can be added just before application to give very long pot life.

4.1. Use of conventional blocked isocyanates

The most straightforward way to get blocked isocyanates into water is through physical incorporation. The blocked isocyanate can be stirred into a waterborne coreactant; however, the high viscosity of the blocked isocyanate makes this difficult. Reducing the viscosity by dissolving the blocked isocyanate with a solvent such as butyl glycol permits easier incorporation but increases VOC [7].

Surfactants can be used to emulsify a blocked isocyanate and adding the emulsion to a waterborne system. For example, an emulsion can be made of MDI partially reacted with 1,3-butanediol then blocked with MEKO [8] and an emulsion of MEKO blocked MDI is added as a cross-linker to a water solution of poly(vinyl alcohol) [4]. An MEKO blocked TDI prepolymer with polytetramethyleneether glycol and bis(4-aminophenyl)methane emulsion with a surfactant is used to make polyurethane elastomers [9]. A non-ionic surfactant terminated with a bisulfite blocked isocyanate made by reacting polyethoxylated nonylphenol with hexamethylene diisocyanate (HDI) and then blocking is used as a surfactant for MEKO blocked HDI biuret [10]. When used as a cross-linker for a polyol, water resistance of films was much superior to a comparative film made using just the nonylphenol non-ionic surfactant as emulsifier.

Achieving mechanical stability of the emulsion requires that viscosity of the blocked isocyanate be relatively low but the viscosity of widely used blocked isocyanates like MEKO blocked HDI and IPDI isocyanurates is relatively high [5]. One approach to emulsifying these blocked isocyanates is to dilute them with a co-reactive solvent such 1,4-butanediol [5]. Also non-reactive solvents such as aromatic hydrocarbons have been used. A way of emulsifying solvent free MEKO blocked HDI isocyanurate ($\eta = 3.5 \text{ Pa} \cdot \text{s}$) is to emulsify with using a high internal phase ratio [11]. At a high internal phase ratio the emulsion is highly shear thinning, in local volumes the particles are exposed to high shear leading to their disruption; after the emulsification stage water is added to give the desired solids and final viscosity. Ref. [11] also provides a discussion of the factors controlling particle sizes of emulsions. Optimization of process variables in emulsification of MEKO blocked isocyanate-terminated polyols is also discussed in [12].

Blocked isocyanate acrylic powder coatings can be dispersed in water for conventional spray application [13]. (See Section 5.1.5 for other examples of water-dispersed powder coatings.)

Encapsulated polyisocyanates solid particles (Fig. 1) (see Section 3.11) can be dispersed in waterborne systems. For example, dispersions of encapsulated TDI uretdione have been added as cross-linkers to hydroxy-functional acrylic latexes in textile print colors [14].

Blocked isocyanates can be incorporated directly into aqueous polyurethane dispersions (PUDs) or into water-reducible resins before dispersion in water to serve as cross-linkers for hydroxyl, amine and/or carboxylic acid groups. The aggregates are stabilized by the hydrophilic salt groups on the surface of the aggregates as shown in



Fig. 1. Isocyanate encapsulation and breakage.

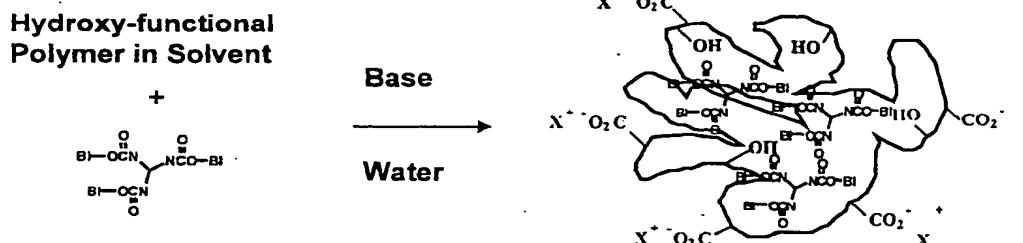


Fig. 2. Dispersion of blocked isocyanate within polymer aggregates in water.

Fig. 2. The blocked isocyanate dissolves in the hydrophobic interior of the aggregates. Usually the aqueous dispersion is made and then the blocked isocyanate is added to it. However, polymerization of ethyl acrylate, HEA, styrene, and acrylic acid to make the acrylic resin can be carried out in a solution of ethyl alcohol blocked IPDI, neutralized with 2-N,N-dimethylaminoethyl alcohol (DMAE) to give a low VOC, HAP-free coating system [15]. (HAP is the acronym used for hazardous air pollutants, a class of chemicals that the US Environmental Protection Agency has targeted for substantial reductions in their emission.) The same patent discloses a cationic system that uses DMAE methacrylate as a comonomer instead of acrylic acid and is neutralized with lactic acid.

MEKO blocked hydrogenated MDI ($H_{12}MDI$) [3] and MEKO blocked HDI/trimethylolpropane (TMP) prepolymer [16] have been used as cross-linkers for PUDs. Factors controlling particle size and stability of emulsions of blocked isocyanates for use as cross-linkers for PUDs has been investigated [11]. Another approach to making anionically stabilized PUDs bearing blocked isocyanates, uses an adduct of acrylic acid and ethylene diamine for chain extension of a polyurethane with an MDI propoxylated TMP and polypropylene glycol prepolymer partially blocked with MEKO [17]. Blocked isocyanate PUDs that self-cross-link are made by reacting HDI isocyanurate with a monobutylether of a polyether polyol and blocking with MEKO, then adding the sodium salt of lysine, diethanolamine, and a primary diamine [18].

Mixtures of high hexamethoxymethylmelamine (HMMM) content melamine-formaldehyde (MF) resins and MEKO blocked IPDI can be used as cross-linkers for water-reducible trialkoxysilyl-functional acrylic (and other) resins [19].

Thermosetting cationically stabilized acrylic latexes have been prepared using cationic surfactants with phosphate gegen ions, acrylic and methacrylic esters, 2-hydroxypropyl methacrylate, DMAE methacrylate incorporating IPDI blocked with di-n-butylamine and DMAE [20].

4.2. Use of water-dispersible blocked isocyanates

Incorporation of blocked isocyanates into an aqueous dispersion of coreactant is facilitated by making water-dispersible blocked isocyanates. This avoids the need to add

emulsifying agents to the system. Several approaches have been investigated.

4.2.1. Use of blocking groups that impart water dispersibility

Water-dispersible sodium bisulfite blocked polyisocyanates are commonly called water soluble (see Section 4.2.4). Bisulfite adducts are prepared by reacting aqueous solutions of sodium bisulfite, $NaHSO_3$ (or sodium pyrosulfite, $Na_2S_2O_5$ with $NaHCO_3$) with isocyanates. They have been used particularly in textile, paper, and leather treatments (See Section 7) with a wide variety of coreactants; on textiles, e.g., the reaction proceeds rapidly by steaming at 103°C or dry heat at 130°C [21]. In some cases, the coreactants bear fluorine substituents for water/oil repellency. In others, the coreactant is the substrate, e.g., wool treatments in which the blocked isocyanate reacts with amine groups on the protein of the wool. Stability of water solutions is greater for aliphatic than aromatic blocked isocyanates but a process has been devised to make aromatic derivatives (see Section 3.9) [22]. They deblock at lower temperatures and have been patented for use in jute reinforced plastics (see Section 8.2). Water-dispersible resins are made by bisulfite blocking of an NCO-terminated HDI polyester diol TMP resin [23]. Water-dispersible blocked isocyanates have been prepared by reacting HDI isocyanurate with a polyether diol and *N*-(2-hydroxyethyl)morpholine with dimethyl sulfate to give a product with quaternary amine salt groups and blocking the remaining isocyanate groups with sodium bisulfite [24]. In the same patent another product was made by reacting HDI trimer with a polyether diol, polyether triol, a sulfonate diol made by reacting 2,2-dimethylethane sulfonate salt and then blocking the remaining isocyanate groups with sodium bisulfite.

Meldrum's acid blocked isocyanates are so acidic that the first reaction with an amine is neutralization (Fig. 3) [25]. This permits formulation of storage stable anionic hydroxy-functional waterborne coatings. When heated the amine volatilizes and cross-linking occurs.

4.2.2. Ionically modified blocked isocyanates

A process for manufacturing emulsions of blocked isocyanates such as the triethylamine (TEA) salt of MEKO blocked HDI polyisocyanate partially reacted with polyoxyethyl-

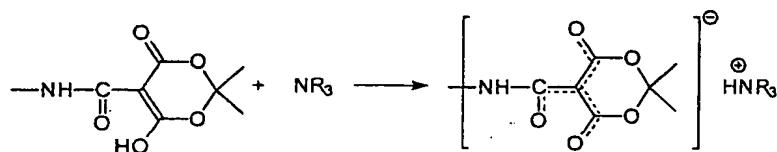


Fig. 3. Formation of amine salt of Meldrum's acid blocked isocyanate.

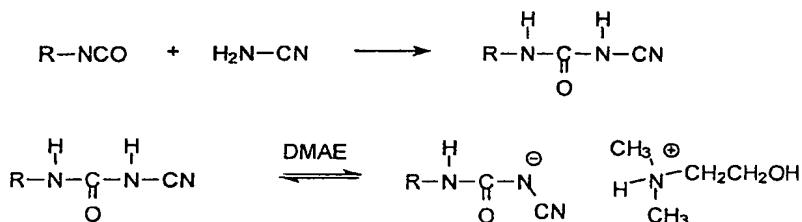


Fig. 4. Formation of an amine salt of a cyanurea formed by the reaction of cyanamide with an isocyanate.

nonylphenol ether phosphate has been patented [12]. HDI isocyanurate partially reacted with a monobutylether of a polyglycol and the sodium salt of 2-aminoethyl-2-aminopropionic acid is blocked with MEKO to give a water-dispersible blocked polyisocyanate [26].

An anionic water-dispersible polyisocyanate is made by reacting partially MEKO blocked HDI isocyanurate with cyanamide and neutralizing the cyanurea with DMAE to form a salt [27]. The product has the advantage that when used as a cross-linker for a thermosetting water-reducible acrylic resin, not only do the isocyanate groups released by deblocking cross-link the coating, but also additional cross-links come from reactions of the cyanurea groups with each other after the amine (Fig. 4) volatilizes from the film. Furthermore, the solubilizing groups are now cross-linked and not present to decrease water resistance of the films.

An anionically modified version of HDI isocyanurate blocked with MEKO can be prepared by reacting the major-

rity of the isocyanate groups with MEKO and subsequently reacting with DMPA; amine salts of the compound are water dispersible (Fig. 5) [28-31]. A combination of IPDI isocyanurate and IPDI in acetone is partially reacted with 2,2-dimethylolpropionic acid (DMPA) and the remaining isocyanate groups blocked with MEKO, *N,N*-diethylaminoethanol is added and the solution diluted with water, evaporation of the acetone gives a stable aqueous dispersion [32].

Partially blocked isocyanates, such as DEM blocked HDI biuret, can be further reacted with the sodium salt of 2-(2-aminoethylamino)ethane sulfonic (and optionally a monobutyl ether of polyethylene glycol) to form a water-dispersible blocked isocyanate used as a cross-linker for a water-reducible polyester [33].

Cationically stabilized water-dispersible blocked isocyanates have also been investigated. 2-Dimethylaminomethylphenol with HDI isocyanurate gives a blocked isocyanate

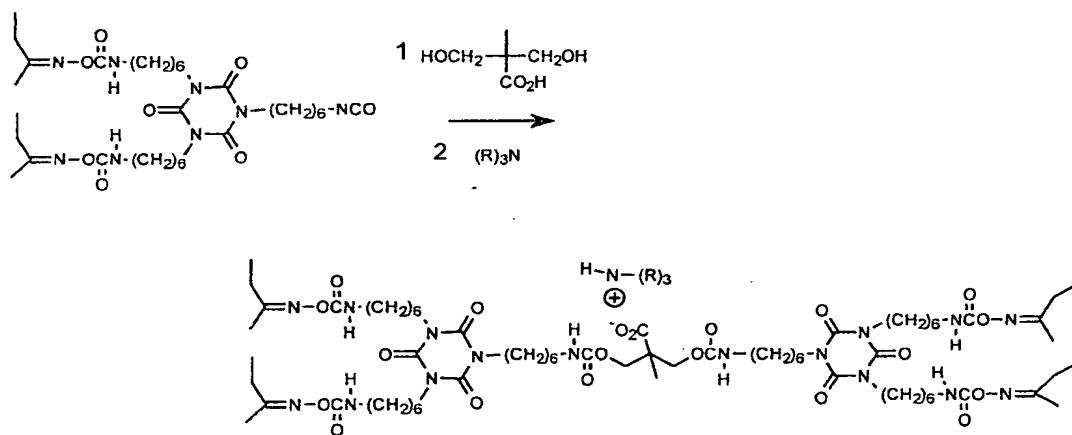
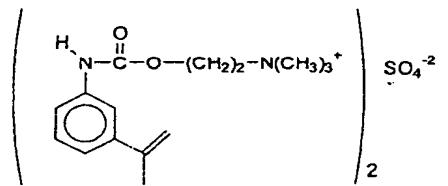


Fig. 5. Use of the amine salt of DMPA to form a water-dispersible MEKO blocked HDI isocyanurate.

that is water dispersible as its acetate salt [34]. Phosphoric acid salts of 2-isopropylimidazole blocked HDI isocyanurate/polyether polyols are water dispersible [35]. α -Dimethylamino- ϵ -caprolactam blocked MDI neutralized with formic acid has been used as a cross-linker with a hydroxy-functional acrylic [36]. A waterborne blocked isocyanates are made with taurine salts or sodium glycinate as a coreactant in their preparation, e.g., water dispersible a blocked TDI/TMP and 1,4-butanediol prepolymer is made by reacting part of the free isocyanate groups with taurine (2-aminoethyl sulfonic acid) and the balance with phenol [37]. A copolymer of TMI blocked with 2-(trimethylammonium)ethyl alcohol sulfate and acrylamide gives a water-soluble polymer for use in paper treatments [38].

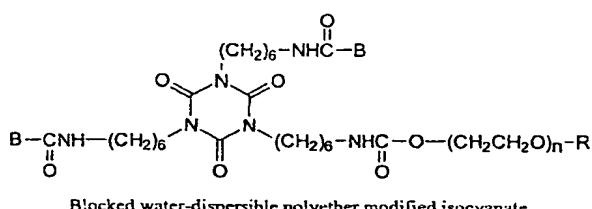


2-(Trimethylammonium)ethyl alcohol blocked TMI sulfate

4.2.3. Non-ionically modified water-dispersible blocked isocyanates

Water-dispersible blocked isocyanates can also be made by reaction of an isocyanate group with the monoether of a polyglycol then blocking the remaining isocyanate groups. For example, HDI is partially reacted with 1,3-butanediol, trimerized, partially reacted with a monomethyl ether of polyethylene glycol, and blocked with MEKO [39]. Modifying a polyisocyanate with a monoether of a polyglycol and then blocking is reported as another approach to obtain stable small particle size emulsions. For example, an HDI adduct of 1,3-butanediol has been trimerized then partially reacted with a monomethyl ether of a polyethylene glycol followed by blocking with MEKO, the blocked isocyanate gives stable aqueous dispersions [40]. MDI is partially reacted with a monobutyl ether of polyethylene glycol/polypropylene glycol and butanediol then blocked with MEKO [41], an HDI adduct reacted with a methyl ether of polyethylene glycol and blocked with CL [42], and HDI isocyanurate is reacted with a monomethyl ether of polyethylene glycol and MEKO [43] to form water-dispersible blocked isocyanates. A polyether polyol is reacted with HDI to give a prepolymer with an average isocyanate functionality of 5.3, then with a polyethylene glycol monomethyl ether, and finally the terminal isocyanate groups are blocked with MEKO to give a water-dispersible blocked isocyanate [44]. H₁₂MDI is partially reacted with a monomethyl ether of polyethylene glycol, partially blocked with MEKO and then reacted with isophoronediamine (IPDA) and adipic acid dihydrazide [45]. A DMP blocked HDI isocyanurate prepolymer with a polyalkylene oxide diamine with a surfactant forms a

stable aqueous dispersion [46]. Rather than preparing a water-dispersible isocyanate from an isocyanurate, one can trimerize a water-reducible monomeric isocyanate. For example, MDI can be partially reacted with the monobutyl ether of a polyether glycol in water, blocked with MEKO, and then trimerized [47]. An MEKO blocked isocyanate reacted with the monomethyl ether of a polyether polyol is used as a cross-linker for water-reducible acrylic resins [48]. Partially blocked 4-isocyanato-1,8-octamethylene diisocyanate is reacted with a methyl ether of a polyethylene glycol to give a water-dispersible blocked isocyanate [49].



Blocked water-dispersible polyether modified isocyanate

Uretdiones have also been used in making high functionality, low viscosity, water-dispersible blocked isocyanates; e.g., a combination of HDI uretdione and isocyanurate are reacted with the methyl ether of a polyethylene glycol and neopentylglycol and the residual free isocyanate groups are reacted with 2EH and diluted with water [50]. Waterborne coatings using this dispersion are cross-linked with ethylene diamine; films cure in 14 days at ambient temperature.

In a study comparing the use of a water-dispersible MEKO blocked H₁₂MDI prepolymer versus one with blocked IPDI with a hydroxy-functional PUD in coatings for glass; it was found, in general, that H₁₂MDI gave better performance than IPDI [51]. A PUD prepared from a polyester-polycarbonate, IPDI, and DMPA, neutralized with DMAE and dispersed in water is cross-linked with a water-dispersible MEKO blocked isocyanate [52]. 3,5-Dimethylpyrazole (DMP) blocked HDI isocyanurate modified, so that it readily emulsifies in a hydroxy-functional acrylic latex has been suggested as a binder for clear coats [53]. An emulsion of an alkyltin mercaptide is used as catalyst since the hydrolytic stability of dibutyltin dilaurate (DBTDL) is inadequate.

A waterborne coating is formulated with an aqueous dispersion of MEKO blocked HDI isocyanurate reacted with DMPA and a hydroxy-functional PUD with an epoxy resin [54]. The same aqueous dispersion of blocked isocyanate is used with a hydroxy-functional PUD chain extended with a mixture of ethylenediamine, IPDA, and diethylenetriamine (DETA) and an epoxy resin emulsion gives improved humidity resistance [55]. A nonylphenol blocked TDI prepolymer with polyalkyleneoxylated glycerol, and butyl alcohol is used to cross-link a waterborne epoxy resin and bis(4-amino-3-methylcyclohexyl)methane [56].

4.2.4. Blocked isocyanate-functional water-dispersible resins

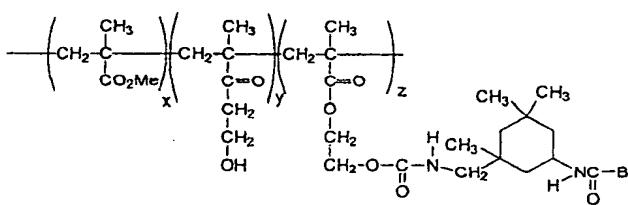
PUDs with MEKO blocked oligomeric MDI terminal groups have been studied [57]. The dispersions were made by reacting polypropylene glycol, DMPA, oligomeric MDI in *N*-methylpyrrolidone (NMP) and acetone after the polymerization the terminal NCO groups were blocked with MEKO, the resin neutralized with TEA, diluted with water and the acetone distilled out of the dispersion. The dispersions can be cross-linked with a stoichiometric amount of tetraethylenepentamine (TEPA) at 110°C. Dispersions containing TEPA showed storage stability of at least 6 months; however, if hexamethylenediamine was used instead of TEPA, stability was less than 1 week. An anionically stabilized PUD in which the remaining IPDI isocyanate groups are blocked with CL has been used to make a thermosetting waterborne coating with an anionic PUD made using HDI as the diisocyanate [58]. A phenol blocked isocyanate-terminated anionic PUD solubilized with taurine can be cross-linked with polyamines [59]. A PUD prepared from a polyester diol, propoxylated TMP, a monobutyl ether of ethylene glycol, DMPA, MEKO, MDI, and chain extended with bis(4-amino-3-methylcyclohexyl)methane has been patented [60]. PUDs with both MEKO blocked isocyanate groups and hydroxyl groups have been used with diamines in the preparation of synthetic leathers [61]. A uretdione functional PUD is prepared by reacting a polyester diol with IPDI uretdione, chain extending with IPDA, reacting with aminocaproic acid to provide the stabilizing COOH group and dispersing in water [62]. The PUD can be used to cross-link polyols. Another approach is the preparation of malonic ester blocked isocyanate-terminated PUDs [63]. A self-cross-linking PUD is prepared by reacting a polyester diol, TMP, DMPA, TEA, H₁₂MDI, and MEKO blocked HDI isocyanurate [64].

Blocked isocyanates have also been used to prepare amine-terminated PUDs. An MEKO blocked TDI prepolymer prepared with DMPA and a polyester diol is reacted with aminoethylmethanolamine then dispersed in water; the product is used as a cross-linker for bisphenol A (BPA) epoxy resin adhesives [65]. CL half-blocked TDI is reacted with a polyurethane made from polypropylene glycol, MDI, and the resulting product is reacted with triethylenetetramine and dispersed in water with an acid neutralizer to prepare an amine-terminated PUD [66].

Blocked TMI, (meth)acrylic acid, HEA, and other acrylic ester monomer copolymers have been used to prepare water-reducible, self-cross-linking acrylic resins [67]. A low molecular weight 2-isocyanatoethyl methacrylate (IEM) acrylic polymer can be reacted with HEMA and MEKO, then copolymerized to give a water-reducible acrylic [68]. Similarly, a macromonomer can be made by copolymerizing TMI and butyl acrylate, followed by blocking part of the NCO groups with MEKO and reacting the remaining NCO groups with HEMA. This macromonomer can then be used to make a graft copolymer with acrylate esters, HEMA,

and acrylic acid followed by blocking any unreacted NCO groups with MEKO. Amine salts of the acrylic copolymer are a self-cross-linkable water-reducible copolymer [69]. With DMAE methacrylate instead of acrylic acid in the graft copolymerization step, one can make the corresponding cationic water-reducible graft copolymers. A graft copolymer made from an MEKO blocked TMI hydroxy-functional acrylic resin grafted with another acrylic made from HEA and dimethylaminopropyl methacrylate is neutralized with acetic acid to make a self-cross-linking resin for waterborne coatings [70].

Oxime blocked isocyanate-functional acrylic monomers such as IEM [71] and TMI [72–75] have been used as a comonomer in making acrylic latexes. Acrylonitrile/butadiene latexes using CL blocked TMI as a comonomer have been patented [76]. Thermosetting acrylic latexes can also be made using HEA or HEMA reacted with one NCO group on a diisocyanate and blocking the other NCO group as a comonomer with other acrylic monomers, including HEA, or HEMA, and/or acrylic acid to serve as a cross-linking site. Examples of such monomers are those derived by reacting MEKO with the product of 1 mol of IPDI and 1 mol of HEMA [77,78], IPDI with HEA [79], MEKO blocked product from HDI isocyanurate and HEMA [80], MEKO blocked reaction product of HEMA with *m*-tetramethylxylylene diisocyanate (TMXDI) TMP prepolymer [81], and sodium bisulfite blocked reaction product of HEMA with HDI-terminated propylene glycol [82]. Alcohol blocked isocyanates are made by reacting IPDI with HEMA and hydroxypropyl carbamate (see Addendum, Section 3.2), the blocked isocyanate monomer can be copolymerized with other (meth)acrylates, HEMA, and acrylic acid to form a self-cross-linking water-reducible acrylic resin [83]. The same type of monomer can be used in preparing acrylic latexes.



Blocked isocyanate acrylic copolymer

Silicone emulsions with good stability that yield tough coatings are prepared by emulsion polymerization of cyclic diorganopolysiloxanes such as octamethylcyclotetrasiloxane and MEKO blocked 2-isocyanatopropyltrimethoxysilane [84].

4.3. Use of blocked isocyanates in synthesizing polyurethane dispersions

Most of the uses of blocked isocyanates in waterborne coatings have been for thermosetting coatings but blocked

isocyanates have been used in preparing thermoplastic PUDs. The chain extension step of the isocyanate-terminated polyurethane in their preparation is made uniform by blocking the terminal isocyanate groups before diluting with water. A blocked isocyanate is made from DMFA, polytetramethylene ether glycol, MEKO, and trimethylhexamethylene diisocyanate. After heating to complete the reaction, the blocked isocyanate prepolymer is diluted with acetone, DMAE is added and a dispersion made by diluting with water and then chain extended with a mixture of IPDA and DETA, finally the acetone and methyl ethyl ketone (MEK) are distilled off [85]. Due to the presence of some cross-linking, the film obtained is quite resistant to solvents. Harder films can be obtained using MDI as the isocyanate but then the films have to be heated to achieve full coalescence. Another approach is the preparation of malonic ester blocked isocyanate-terminated PUDs [86]. A PUD with DEM blocked isocyanate substituents is made from IPDI/polyester polyols and 1,4-butanediol, blocked with DEM, chain extended with *N*-methyldiethanolamine, neutralized with HCl and dispersed in water [87].

An anionically modified prepolymer with MEKO blocked terminal isocyanate groups is mixed with a polyamine and then dispersed in water. The aqueous dispersion is heated to carry out the chain extension reaction between the blocked isocyanate groups and the amines. After diluting with water, the chain extending amine is added and dissolves in the polymer particles. There it reacts with the blocked isocyanate groups releasing blocking agent and forming a relatively uniform polymer. Alternatively, an excess of polyamine with more than two amine groups can be reacted with a blocked diisocyanate, then added to the solution of the prepolymer. The unreacted amine groups are neutralized with acid, and the resin is dispersed in water [88].

Cationic PUDs have also been made using a blocked isocyanate to control the reactions. TDI polyether polyol is blocked with MEKO, DETA is added, the polymer is then dispersed in acetic acid containing water [89].

4.4. Catalysis of waterborne blocked isocyanate systems

Catalysis of reactions of blocked isocyanate hydroxyl reactions in waterborne systems requires special consideration that has not apparently been widely recognized except in cationic E-coats. It is well known that carboxylic acids inhibit catalysis by organotin compounds and most waterborne systems include coreactants that are dispersed in water by amine salts of carboxylic acid groups on the resin. Blocked isocyanate anionic coatings are catalyzed to a lesser degree by DBTDL than the corresponding 2K solvent-borne coating and require higher curing temperature (or longer time) to reach the same extent of cross-linking [5]. It was demonstrated that the cure rate of such coatings was affected by the acid number of the coreactant coatings with higher acid number coreactants cured more slowly with the same level of catalyst. Another paper reports

that DBTDL does not catalyze the cure of waterborne coatings [7].

Another factor affecting catalysis is the hydrolytic stability of the catalyst. DBTDL is relatively easily hydrolyzed, hence is a poor choice although it is commonly reported as the catalyst. Mercapto derivatives of tin catalysts are reported to be more stable to hydrolysis and more effective as catalysts for anionic systems [5,53].

In cationic systems, there is no problem with carboxylic acid inhibition since the acid used to neutralize the amine is volatilized before the unblocking reaction and indeed, the amine group on the coreactant may well catalyze the reaction of isocyanate with hydroxyl groups. In cationic E-coatings, the problem of hydrolytic stability of the catalyst has been widely recognized and studied (see Section 5.3.3).

5. Uses for blocked isocyanates in coatings

Blocked isocyanates have the distinct advantage that one package (1K) coatings can be formulated with them. 1K coatings have many advantages over 2K coatings: the risk that improper ratios of the two components will be mixed is eliminated, handling and capital costs for the applicator are reduced, waste resulting from mixing an amount of 2K formulations larger than can be used within the pot life time span is reduced, and toxic hazard is significantly reduced. In many cases, 1K coatings fully match the performance properties of their 2K counterparts. On the other hand, higher temperatures for curing are required, the energy costs thus increase and heat-sensitive substrates, such as some plastics, cannot be coated, and in some cases the blocking agents have toxic hazards. With highly reactive primary diamines, 2 K solvent systems have too short pot lives to be useful but they can be used in ambient cure 2K coatings with blocked polyisocyanates.

5.1. Powder coatings

Powder coatings are a rapidly expanding part of the coatings industry because of low VOC emissions. Blocked isocyanates are widely used as cross-linkers in powder coatings, particularly in North America and Asia. Usage in Europe, while sizeable, has been smaller. But the situation in Europe may be changing since concern has been expressed about the toxicity of triglycidyl isocyanurate, which has been widely used as a cross-linking agent, especially in Europe. Many types of materials are used in powder coatings, polyurethane coatings are used when excellent exterior durability is required. Therefore, principally blocked aliphatic isocyanates are used; there are, however, applications where exterior durability is not important, in those cases aromatic isocyanates may be used. Curing of powder coatings using IR ovens instead of convection ovens permits faster curing but there are variations in response to IR particularly with different pigments [90]. In addition to

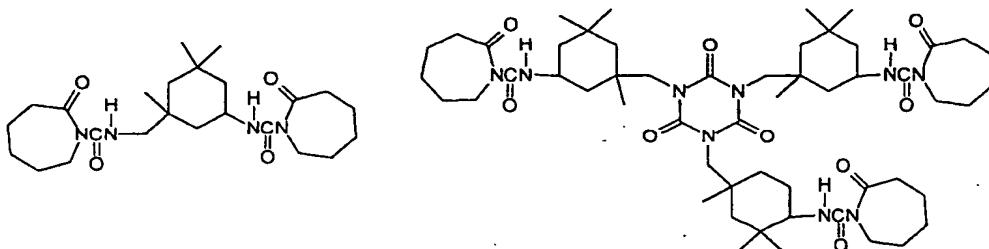


Fig. 6. CL blocked isocyanate monomer and isocyanurate.

the powder coatings discussed in this section, powder coatings for use as clear coats for automobiles are discussed in Section 5.4.1, powder primer coatings for automobiles are covered in Section 5.4.2, an aqueous powder coating for plastics in Section 5.6, powder adhesives are discussed in Section 6.2, and powdered materials are used in making some molded plastics as discussed in Section 8.1.

5.1.1. With lactam blocked isocyanates

For many years the main blocked isocyanate for use with hydroxy-functional polyesters and acrylics has been the CL adduct of a mixture of IPDI and IPDI isocyanurate (Fig. 6). During the period reviewed, there have been many patents issued using such a CL blocked isocyanate, the differences are primarily in the polyol component; [91] is given as one example. In that reference, flow and curing properties of coatings with partially trimerized IPDI blocked with CL and hydroxy-functional acrylic resins are compared with those of acid cross-linked epoxy-functional acrylic resins and hydroxylalkylamide cross-linked carboxylic acid-functional acrylic resins. Heating partially CL blocked IPDI with 1% sodium stearate [92], Mg 2-hydroxyethyl phthalate [93], or dimethyl(2-hydroxypropyl)(2,2,6,6-tetramethylpiperidinyl)-ammonium formate [94] (trimerization catalysts) is a more efficient process for producing the blocked isocyanate for use in polyester/polyurethane powder coatings. A process for continuous production of CL blocked IPDI for use in powder coatings has been patented [95]. CL blocked IPDI polyisocyanate is used with a hydroxy-functional polyester and rubber-resin composite particles to make a powder coating with superior smoothness [96].

Rather than using a mixture of IPDI monomer and trimer, use of a TMP adduct of monomeric IPDI has been suggested as a route to give a similar average functionality [97]. The use of CL blocked IPDI/pentaerythritol prepolymer has also been patented [98]. CL blocked IPDI/diethylene glycol prepolymer or partially trimerized IPDI reacted with a hydroxy-functional polyester blocking with some unreacted NCO groups left unblocked gives stable powders that cure at a somewhat lower temperature [99]. The inventors suggest that the unreacted NCO groups react with hydroxyl groups during melt extrusion of the powder coating.

CL blocked *trans*-cyclohexane-1,4-diisocyanate melts at 210–213°C compared to 53–55°C for the CL blocked IPDI [100]. This higher melt temperature permits use of lower T_g coreactants without encountering sintering of a powder coating during storage. This blocked isocyanate gives powder coatings that cure at 10–20°C lower temperature than CL blocked HDI powder coatings.

Properties can be affected by the free carboxylic acid content of the polyester used with the CL blocked IPDI; higher acid content reduces cure rate, increases yellowing, and decreases salt spray resistance [101]. However, added adipic or benzoic acid increases cure rate. The adverse effects of excess COOH can be overcome by adding an epoxy compound to react with the COOH groups. Coatings having good appearance and no foaming or yellowing when applied as thick films and baked at high temperatures are made using CL blocked IPDI ethylene glycol prepolymer with one of the polyester coreactants is a copolymer-containing *p*-hydroxybenzoic acid glycidyl ester ether modified with terephthalic acid or 5,5-dimethylhydantoin [102].

The patent literature includes examples of many isocyanate products that can be used with CL, in general, these alternatives provide faster curing:

- H₁₂MDI [103–106];
- H₁₂MDI/TMP prepolymer [107];
- a mixture of HDI and IPDI isocyanurates [108];
- HDI/IPDA prepolymers [109];
- xylylene diisocyanate (XDI) [104];
- H₆XDI/TMP prepolymer [110] (hydrogenated xylylene diisocyanate, H₆XDI);
- an isocyanurate from trimerizing a mixed 1,5-diisocyanato-2-methylpentane and 1,4-diisocyanato-2-ethylbutane [111];
- a mixture of trimers of 1,5-diisocyanato-2-methylpentane and 4-diisocyanato-2-ethylbutane with IPDI [112,113];
- vinyl isocyanate-containing acrylic copolymers [114];
- mixed 5- and 6-isocyanato-1-(4'-isocyanatophenyl)-1,3,3-trimethylindane [115];
- TMXDI [104,116];
- norbornane diisocyanate [117];
- methylene diisocyanate (see Addendum, Section 3.4) [118];

- pyrrolidone urea adduct of HMMM (see Addendum, Section 3.9) [119].

CL blocked $H_{12}MDI$ that has been reacted with a small fraction of *n*-butyl alcohol to partially convert the isocyanate groups to urethanes and reacted with sufficient perfluoropropylene glycol monoethers to incorporate about 0.5% of fluorine in the compound are used to cross-link hydroxy-functional acrylic powder coatings [120]. The combination of fluorine content and partial conversion to urethanes lowers the melt viscosity permitting better flow. A powder coating with superior flow is formulated with CL blocked $H_{12}MDI$, 1,6-hexanediol, hydroxy-functional acrylic, and polyester resins [121].

Mixed HDI-IPDI half-blocked with CL [122], HDI half-blocked with CL and a small amount of dimethylhydrazine with a hydroxy-terminated polyester are reported to give less discoloration during baking than coatings without the IPDI or the dimethylhydrazine [123]. Yellowing has been reduced using a CL blocked IPDI partial adduct with 4-bis(hydroxyethylamino)-2,2,6,6-tetramethylpiperidine [124].

A combination of two hydroxy-functional acrylic resins, one of which is made with perfluoroalkyl acrylates is used with a blocked isocyanate to give a coating with outstanding exterior durability [125].

Poor exterior durability limits the usefulness of aromatic isocyanates but they do react at lower temperatures. For example, CL blocked TDI gives faster curing but severe yellowing on exterior exposure [126].

Silicone-modified polyesters can be cross-linked with CL blocked IPDI [127]. Silicone resins with CL blocked IPDI isocyanurate have been used as binders for high temperature resistant coatings [128]. Styrene/allyl alcohol copolymers have been recommended for partial replacement of hydroxy-functional polyesters in powder coatings using CL blocked IPDI oligomer as a cross-linker [129]. The adhesion of a polyamide powder coating is improved by adding 1% of CL blocked IPDI to an amine-terminated polylaurolactam [130].

A process for manufacturing powder coatings not requiring extrusion has been patented; a CL blocked partially trimerized IPDI and a hydroxy-functional polyester are dispersed in water using a surfactant, milled, and dried [131]. Another approach to manufacturing without extrusion is to spray dry a solvent solution of the vehicle [132]. Thus, a solution of hydroxy-functional acrylic resin, CL blocked partially trimerized IPDI, MF resin, and additives in MEK is spray dried at 120°C, no sintering was found after 2 weeks at 30°C.

5.1.2. Other volatile blocking agents

In general, CL blocked isocyanate powder coatings show good package stability, good leveling, and excellent performance. The good leveling is a result of favorable rheological behavior at melt temperatures and because part of the caprolactam remains in the film [106]. However,

high temperature cures are required, yellowing can occur at these high temperatures, the evolved caprolactam leads to oven fouling particularly of the oven gas outlet tubes, and caprolactam is on the HAPs list. A variety of other blocking agents have been investigated as replacements; a useful replacement must at least maintain the package stability, good leveling, and performance, while reducing cure temperature with a blocking agent that is non-toxic.

4-Hydroxybenzoate esters have been used to block HDI isocyanurate; when used with hydroxy-functional polyesters, powder coatings are formulated which cure at lower temperatures than CL blocked IPDI to give films that are more flexible [133,134]. Use of a mixture of 4-hydroxybenzoic acid and its methyl ester blocked HDI isocyanurate has been recommended; the melting point is increased reducing problems of sintering [135]. Use of partially methyl 4-hydroxybenzoate blocked HDI isocyanurate reduces cure temperature as compared with the fully blocked polyisocyanate [136]. HDI isocyanurate blocked with a combination of *p*-hydroxybenzoic acid and its methyl ester gives coatings with lower cure temperature, greater flexibility, and improved exterior durability as compared to conventional blocked IPDI cross-linked coatings [137]. Use of several other phenol and alcohol blocking agents has been patented: methyl hydroxyisobutyrate blocked HDI [138], thymol blocked HDI [139], *p-t*-octylphenol blocked $H_{12}MDI$ -bisphenol. A prepolymer [140], ethyl alcohol blocked dodecane diisocyanate [141], and benzyl alcohol blocked XDI TMP prepolymer [142]. TTI blocked with benzyl alcohol has been reported to cure more rapidly in powder coatings than CL blocked oligomeric IPDI and has the advantages of lower volatile emissions, better flow, and avoiding the problem of clogging pipes encountered with the latter [143]. HDI isocyanurate partially blocked with 3-methyl-1-phenylpyrazalone permits low cure temperatures [144]. The mixed methyl butyl alcohol blocked triisocyanate tris(alkoxycarbonylamino)triazine (TACT) is used as a cross-linker with BPA epoxy resins or glycidyl methacrylate-containing acrylic resins using tetrabutyl-diaceoxydistannoxane as catalyst in 20 min at 150°C (see Section 2.2.2) [145]. Tris(succinimido)-1,3,5-triazine or its prepolymer with TMP with a hydroxy-functional polyester polyol cures in 20 min at 150°C and it has the advantage that there are no volatile byproducts [146].

Ketoximes have been investigated as potential blocking agents. There is, however, concern about toxicity of oximes and yellowing of films. Also MEKO blocked compounds require very careful control of baking conditions and coatings can blister [106].

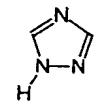
Use of MEKO blocked $H_{12}MDI$ [104,106], MEKO blocked $H_{12}MDI$ polyester polyol prepolymer [147], cyclohexanone oxime blocked $H_{12}MDI$ [106], MEKO blocked HDI isocyanurate or biuret [148], MEKO blocked HDI TMP prepolymer [149], MEKO blocked H_6XDI [149], and MEKO [106], acetone oxime [150], acetophenone oxime [151,152], or 2,6-dimethyl-4-heptanone oxime [153]

blocked IPDI isocyanurate, have been suggested. An MEKO blocked isocyanate prepared by polymerizing the MEKO adduct of HEMA with other acrylic monomers has been patented for use in powder coatings [154]. Superior flow powder coatings are formulated with MEKO blocked HDI biuret and hydroxy-functional polyester and acrylic resins [155]. Methyl isobutyl ketoxime blocked 1,4-bis(isocyanatomethyl)cyclohexane is reported to give powder coatings that cure at lower temperatures than CL blocked IPDI isocyanurate [156]. Since steric hindrance leads to lower deblocking temperatures, acetone oxime blocked TMXDI has been reported to give lower cure temperatures [157]. Branched chain oximes give TMXDI blocked isocyanates with still lower deblocking temperatures (see Table 6 in Section 3.3 in Paper A) [158]. Use of 2,4-dimethyl-3-pentanone oxime and 2,6-dimethyl-4-heptanone oxime blocked TMXDI have been patented [159]. MEKO blocked TMXDI prepolymer with TMP and a polyester polyol has also been used [160]. An MEKO blocked HDI HEMA monomer is copolymerized with other acrylate monomers including HEMA to give a self-cross-linking binder for powder coatings [161].

A self-cross-linking resin for powder coating is prepared from epoxy- and hydroxy-functional acrylic resins by reacting with half-MEKO-blocked IPDI with the hydroxyl groups; the coatings are formulated with dodecyltrimethylammonium iodide catalyst and baked at 185°C for 25 min [162]. The coating is said to cross-link by reaction of epoxy groups with isocyanate groups to form oxazolidones.

1,2,4-Triazole is said to be a promising blocking agent for powder coatings. 1,2,4-Triazole blocked IPDI has been found to give satisfactory film properties at lower curing temperatures and with reduced blocking agent emission [163–165]; good flow properties were obtained by using specially designed polyesters. 1,2,4-Triazole blocked H₁₂MDI has been patented for use in powder coatings [166]. 1,2,4-Triazole blocked H₁₂MDI and IPDI have been compared; the H₁₂MDI product cures at 20°C lower temperature [106]. Flow properties of powder coatings of triazole blocked H₁₂MDI isocyanurate are improved by trimerizing the partially blocked diisocyanates [167]. Triazole blocked mixed HDI and HDI isocyanurate is a solid permitting preparation of stable powders, which cure at low temperatures, whereas MEKO gives liquid blocked isocyanates [168]. Preparation and use of 1,2,4-triazole blocked mixed isocyanates such as HDI isocyanurate and IPDI has been patented [169]. HDI isocyanurate blocked with a mixture of MEKO and 1,2,4-triazole permits formulation of powder coatings with good storage stability and low curing temperature [170]. It is also reported that HDI isocyanurate partially blocked with 1,2,4-triazole has a T_g of 34°C and is useful in powder coatings in contrast to HDI isocyanurate fully blocked with 1,2,4-triazole which has a T_g of 10°C, too low to make storage stable powders [171]. Use of HDI permits more flexible coatings than are possible with IPDI or IPDI trimer. 1,2,4-Triazole blocked IPDI/TMP

prepolymer has been patented for use in powder coatings [172]. Use of a 1,2,4-triazole blocked polyisocyanate with a hydroxy-functional branched polyester for formulating low temperature cure powder coatings has been patented [173].



1,2,4-Triazole

2-Phenylimidazoline blocked IPDI/diethylene glycol prepolymer has been used with hydroxy-functional polyesters [174]. 3,6-Dimethyl-2,5-piperazinedione [175], 3-methyl-1-phenyl-2-pyrazolin-5-one [176], 3,3,6-trimethyl-2-piperazine, and octahydro-3,3-dimethyl-2(1H) quinoxalinone [177] have been patented as blocking agents for powder coatings. 3(5)-Methylpyrazole blocked triphenylmethane triisocyanate has been patented [178].

Several amine blocking agents have been disclosed including 2,6-dimethylpiperidine, dicyclohexylamine, and bis-(3,5,5-trimethylcyclohexyl)amine [179], aziridine blocked 1,3-bis(isocyanatomethyl)cyclohexane [180]. DEM blocked HDI isocyanurate is used as the cross-linker for a trialkoxyalkylsilane- and hydroxy-functional acrylic resin powder coating [181]. Dodecanethiol and *p*-chlorothiophenol blocked TDI have been reported to have low deblocking temperatures [182]. Partially blocked polyisocyanates permit formulation of powder coatings with satisfactory package stability, good flow, and low temperature curing [171].

It has been proposed that low temperature cure powder coatings can be developed in which an acetophenone blocked isocyanate and epoxy-functional coreactant are exposed to UV at temperatures in the region of 100°C [183]. The UV is said to cleave the blocked isocyanate to an amine free radical, and a ketimine free radical which abstract hydrogens to form an amine and a ketimine. The amine reacts with an epoxy group to give a cross-link. The recommended isocyanates are TMI/acrylic ester copolymers and the epoxy resin can be a glycidyl methacrylate copolymer.

5.1.3. Uretdiones in powder coatings

Uretdiones (isocyanate dimers) are made with a phosphine catalyst then terminating the reaction by adding an agent such as methyl *p*-toluenesulfonate. Higher oligomers are also formed. Uretdiones cleave with heat to regenerate isocyanates. IPDI uretdione is reacted with a polyether diol [184–186] to give a “self-blocked isocyanate”. A process has been patented for making an IPDI 2,2,4-trimethylpentane-1,3-diol prepolymer uretdione with tri-*n*-octylphosphine catalyst and terminating the reaction with butanone peroxide to oxidize the phosphine to the corresponding phosphine oxide. This permits recovering excess IPDI by distillation without contamination with the phosphine [187]. A process for making monomeric IPDI uretdione 1,3-butanediol by repeated thin film vacuum distillation has been patented [188].

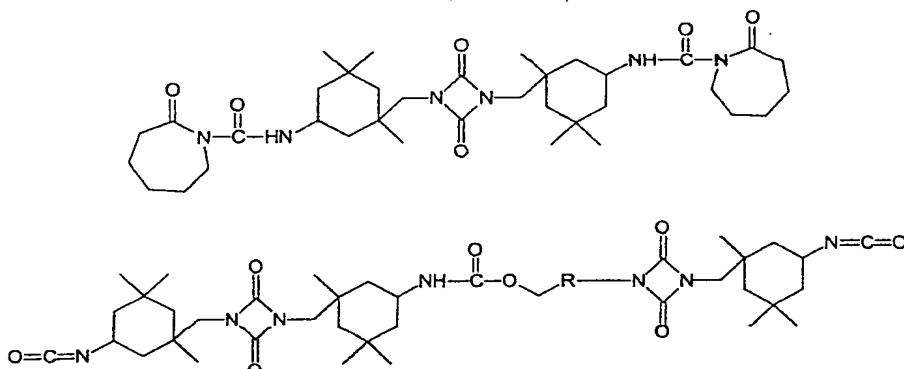
Lighter color uretdiones such as HDI uretdione can be made by using a phosphine such as triphenylphosphine as a color stabilizer during the preparation of the uretdione [189].

The relatively high deblocking temperature of aliphatic uretdiones can be reduced by using amidines, such as 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), or 1,2-dimethyltetrahydropyrimidine, as catalysts [184,185,190].

The free isocyanate groups on IPDI uretdione can be blocked with CL; the amount of CL given off during curing is substantially reduced as compared to CL blocked IPDI isocyanurate systems [191]. Use of CL blocked IPDI uretdione partial adducts with TMP or tris(2-hydroxyethyl)isocyanurate (THEIC) has been patented [192]. Patents have also been issued disclosing use of IPDI uretdione with part of the free isocyanate groups reacted with a butanediol and part with 2EH [193,194] or *n*-butyl alcohol [194]. Melt viscosity is reported to be lower resulting in higher gloss if a polyester, such as hydroxy-functional ester of 1,4-butanediol and caprolactone, instead of a diol like 1,4-butanediol is reacted with IPDI uretdione with the remaining NCO groups blocked with 2EH [195,196]. IPDI uretdione blocked with a variety of diamines or amino alcohols has been patented [197]. IPDI uretdione has been partially reacted with a blocking agent such as CL, dicyclohexylamine, or MEKO then the balance of the NCO groups are reacted with a combination of polyether triols and diols polyester polyol such as a caprolactone diol and triol or TMP and neopentylglycol [198]. In another patent, IPDI uretdione is reacted with a secondary diamine to form a prepolymer and blocking the terminal isocyanate groups with MEKO for cross-linking polyester polyol powder coatings [199].

uretdione a substantial fraction of the HDI is trimerized. A process has been patented for making HDI uretdione with only a small fraction of HDI isocyanurate which is reacted partly with ethylene glycol and partly with ethyl alcohol [201]. Use of a combination of IPDI and HDI permits preparation of a mixed compound with a functionality between 2 and 3, resulting in more rapid cross-linking, furthermore the aliphatic segments increase the flexibility of coatings [202]. A process for dimerizing a 9/1 ratio of HDI/IPDI reacted with 2,2,4-trimethylpentane-1,3-diol has been patented [203]. A mixed HDI/IPDI uretdione blocked with ethyl alcohol has been patented [204]. Uretonimines from IPDI and HDI [205], and a uretonimine derived from H₁₂MDI carbodiimide [206] have been patented for use in powder coatings.

While most of the powder coatings using blocked isocyanates are polyester resin-based, epoxy resin powder coatings have also been cross-linked with blocked isocyanates. In at least some cases the networks are said to include oxazolidinone cross-links (Fig. 7) in addition to urethane networks. Formation of oxazolidinone cross-links is reported in a reaction between the epoxy groups of a BPA epoxy resin and isocyanate released from acetylacetone blocked HDI [207]. The chemical and stain resistance, and surface hardness of BPA epoxy carboxylic-functional polyester powder coatings is markedly increased by incorporating 10% of an IPDI uretdione cross-linker in the powder; there is a reduction in flexibility due to the increased cross-linking [208]. Bicyclic amidines blocked with stearyl isocyanate, HDI, and IPDI [209] and imidazole or imidazoline blocked isocyanate [210] have been used as blocked catalysts for BPA epoxy resin-based powder coatings.



Uretdione with and without blocking

A continuous production process for preparation of uretdione prepolymers has been patented; both blocked and unblocked uretdione examples are given [200]. One of many examples is the continuous production of a CL blocked IPDI uretdione diethylene glycol product.

IPDI uretdione has the limitation that it is only difunctional. When HDI is heated with catalysts to make a

A mixed BPA/carboxylic acid-functional polyester and CL blocked TDI/hydroxy-functional polyester powder coating cures at relatively low temperature [211]. Imidazolines have been used to block polyisocyanates or isocyanate polyol prepolymers formulated with epoxy resins have been patented [212]. 2-Phenylimidazoline blocked IPDI

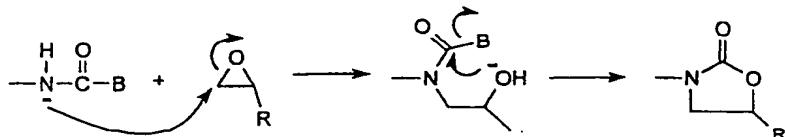


Fig. 7. Reaction of a blocked isocyanate with an epoxy to give an oxazolidinone.

uretdione prepolymer with diols or secondary diamines and the remaining NCO groups blocked have been patented for use in BPA epoxy powder coatings [213]. Powder primers for application in coating junctures of different metals are formulated from a hydroxy-terminated polyester, a carboxy group containing blocked isocyanate, a blocked isocyanate, triglycidyl isocyanurate, and a chlorine containing epoxy resin [214]. Powder coatings to make shatter resistant coatings for glass bottles are made with a substituted hexahydrocyclopentapyrimidine blocked IPDI [215] and 2-phenylimidazoline blocked IPDI or IPDI/diethylene glycol prepolymer [216] with a BPA epoxy resin.

Antibacterial and anti-fungal powder coatings have been formulated with hydroxy-functional polyesters, CL blocked IPDI isocyanurate, and chlorhexidine hydrochloride [217].

5.1.4. Low gloss powder coatings

Another challenge with powder coatings is formulation of low gloss (matte) coatings consistently in production. Various means of controlling gloss are reviewed in [218]. Use of high levels to pigment to reduce gloss as is done in solvent- and waterborne coatings is not feasible with powder coatings since high pigment levels reduce flow. An approach to making lower gloss powder coatings that has been widely used is to add micronized wax to the powder formulation [219]. However, small variations in extrusion conditions affect size of the particles of wax, which makes it difficult to obtain consistent gloss levels. A similar approach is use of powdered protein [220].

Several patents and papers discuss the use of several approaches to formulating low gloss coatings:

- coextrusion of dry blends of two powders having different reactivities;
- use of blocked isocyanates with a fraction of the NCO groups left unreacted;
- using diamine derived prepolymers rather than polyol derived prepolymers;
- using two different coreactants having different reactivities, formulation of a coating with two blocked polyisocyanates having different reactivities;
- combining two different coreactant-cross-linker binders.

In the dry blend process, mixed systems which cross-link at different rates are used; the wider the difference in reactivity, the lower the gloss [218]. For example, use of two polyesters with different hydroxyl content polyesters with an unblocked IPDI uretdione polyether diol prepolymer reduces

gloss in proportion to the ratios of the two polyesters until a minimum gloss is reached at some ratio since the higher functionality polyester gels more rapidly. It was found that curing time also affects gloss with a minimum gloss being reached as full cure is approached but then increasing with longer baking, hence, careful control of curing conditions is required.

CL blocked IPDI with a small fraction of the isocyanate groups left unblocked with hydroxy-functional polyester is reported to give low gloss coatings [221]. The unreacted NCO reacts relatively rapidly giving the differential as compared to the blocked NCO groups.

It has been reported that use of urea containing prepolymers made by reacting the polyisocyanate with a diamine give lower gloss due to incompatibility of the combined system when such prepolymers are used. For example, uretdione cross-linkers chain-extended with diamine rather than diol permit formulation of matte powder coatings [202]. A patent discloses the use of a large number of partially blocked and unblocked uretdiones for use in low gloss powder coatings; one example is IPDI uretdione prepolymer with a diamine prepared from bis(4-aminocyclohexyl)methane and dibutyl maleate [222]. In those cases where partial blocking of NCO was used, the blocking agents were dibutyl amine or 2EH..

Diamine prepolymers and having a fraction of the NCO groups unreacted have been disclosed for use in low gloss coatings. CL blocked IPDI bis(4-aminocyclohexyl)methane (among several amines used) prepolymers with a small fraction of the NCO groups unblocked have been used to cross-link polyesters having an average of 3.5–3.9 hydroxyl groups per molecule. In order to also exhibit good flow properties, the half-blocked IPDI starting material must be almost entirely with only one IPDI and one CL in each molecule, requiring making the blocked compound with a large excess of IPDI which is then removed by thin film vacuum distillation [223]. The dihydrazide obtained by reacting hydrazine hydrate with propylene carbonate (Fig. 8) is used in a CL blocked H₁₂MDI/TMP prepolymer as a cross-linker for low gloss acrylic powder coatings [224].

Powders formulated with two polyesters with different hydroxyl contents provide lower gloss coatings. In this case, after an initial period, gloss during curing remained constant making control of cure time less critical [218]. Use of a mixture of two polyester polyols with different reactivity with CL blocked IPDI isocyanurate [225] or an IPDI uretdione reactant [226] to produce low gloss coatings has

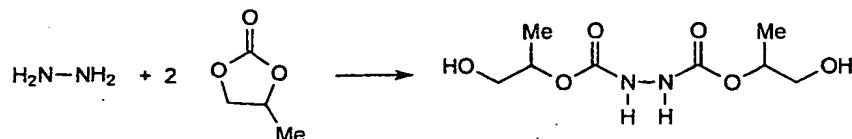


Fig. 8. Reaction of propylene carbonate with hydrazine.

been patented. Use of a combination of an amorphous and a semicrystalline polyesters with CL blocked IPDI polyisocyanate to make low gloss coatings has been patented [227]. Low gloss can also be obtained using a mixture of a semicrystalline polyester polyol and hydroxy-functional acrylic resin with CL blocked IPDI isocyanurate [228]. Low gloss powder coatings have been formulated using HDI isocyanurate blocked with mixed 4-hydroxybenzoic acid and its methyl ester with hydroxy-functional polyesters or acrylics, a catalyst that promotes both the isocyanate reaction and transesterification such as tin oxalate is recommended [229].

Several combinations using two different cross-linkers and two different coreactants have been published. For example, a study of the correlation between the thermal and rheological behavior and gloss of a powder coating consisting of a difunctional polyester resin, glycidyl-functional acrylic resin, a blocked IPDI, dodecanedioic acid, with additives as compared to an epoxy powder coating has been published [230]. In curing the released isocyanate reacts with the hydroxyl groups generated by the reaction of the oxirane ring with the carboxylic acid. Low gloss powder coatings are formulated with a carboxylic acid- and hydroxy-functional polyester, an epoxy-functional acrylic resin, dodecanedioic acid, and CL blocked partially trimerized IPDI [231]. An IPDI uretdione with both blocked terminal isocyanate functionality and carboxylic acid functionality has been formulated with a combination of a hydroxy-terminated polyester to react with the blocked isocyanate and a hydroxylalkylamide or an epoxy-functional coreactant to react with the carboxylic acid groups [218]. Still lower gloss can be obtained by also using some unblocked IPDI uretdione prepolymer or a blocked isocyanate prepolymer in the formulation. Low gloss coatings can be obtained using a combination of polyester polyol, 2EH blocked IPDI uretdione/1,6-hexanediol, TMP prepolymer, a carboxylic acid-terminated resin made from dodecanedioic acid anhydride and HDI isocyanurate, and tetra-*N,N,N',N'*-(2-hydroxyethyl)adipamide [232,233]. Another combination is a polyester polyol, CL blocked IPDI/ethylene glycol prepolymer, dodecanedioic acid, and tetrahydroxyethyl adipamide [234].

2-Phenylimidazoline blocked IPDI ethylene glycol prepolymer with epoxy and epoxy-carboxy polymers have been used to prepare low gloss powder coatings [235]. A combination of BPA epoxy resin, trimellitic acid, and 2-phenylimidazole blocked IPDI also gives low gloss.

Presumably the 2-phenylimidazoline acts not only as a blocking agent but also as a catalyst for the epoxy cross-linking and the IPDI cross-links hydroxyl groups generated in the reaction of the acid and the epoxy resin [236].

CL blocked *trans*-cyclohexane-1,4-diisocyanate isocyanurate prepolymer with 1,12-dodecanediol (among many other diols) is used with high melting point branched polyesters to formulate low gloss powder coatings [237]. It is reported that consistent low gloss coatings can be formulated with HDI isocyanurate blocked with a combination of *p*-hydroxybenzoic acid and its methyl ester [137].

5.1.5. Water-dispersed powder coatings

Some of the problems encountered with powder coatings can be overcome by use of water dispersions of powder coatings. This eliminates the potential problem of explosion of powders. Conventional spray equipment and coating lines can be used. Smaller particle size powders can be used without encountering application problems. The T_g of the powders need not be as high to avoid sintering during storage of the powder, and more flexible coatings can be formulated. Lower curing temperatures are possible since these powders are not made by melt extrusion. Blocked isocyanate acrylic powder coatings can be dispersed in water for conventional spray application [13]. A CL blocked partially trimerized IPDI with a hydroxy-functional isocyanate powder is dispersed in water with surfactants [238]. A graft copolymer of a hydroxy-functional unsaturated polyester resin made with fumaric acid, with a hydroxy- and carboxylic acid-functional acrylic resin in which one of the comonomers is 2-(methacryloyloxy)ethyl dihydrogenphosphate and a blocked isocyanate is used to disperse pigment and then diluted with water. The coarse dispersion is filtered and washed. The powder is then dispersed in water with a dispersing agent and an acrylic water-soluble thickening agent and dispersed in a ball mill, so that the average particle size is 10 μm [239]. Similar coatings have been patented in which a saturated polyester is blended with an phosphate acid modified acrylic resin [240], a saturated polyester with phenolic functionality included by using gallic acid as a comonomer with the same acrylic [241], and with a polyester/acrylic graft polymer with only acrylic acid furnishing the acidic substitution [242]. A cationic hydroxy-functional acrylic water-reducible resin is used with a hydroxy-functional polyester and a blocked isocyanate in formulating a waterborne powder coating [243].

5.2. Coil coatings

For coil coating operations, where the bake temperatures are very high and dwell times are short, there are several challenges to blocked isocyanate-based systems. The high temperatures can lead to discoloration, especially during line stoppages. The short dwell times make it difficult for the blocking groups to volatilize without causing popping. In spite of these difficulties, many patents have been filed for the application and commercial systems are in use.

Several patents have been issued for blocked isocyanates in coil coating primers. CL blocked TDI polypropylene glycol prepolymer is used with a polysulfide-, polyamine-modified epoxy resin in a coil coating primer [244]. Other coil coating primers have been formulated with MEKO blocked polyisocyanate, chlorinated rubber, and a resole phenolic resin [245], MEKO blocked HDI biuret, a hydroxy-functional polyester, BPA epoxy resin, and a phenolic resin [246], CL blocked HDI and a hydroxy-terminated polyester [247], and a blocked isocyanate with a hydroxy-functional urethane resin [248]. A primer made with a polyester, MF resin, and ethyl acetoacetate blocked IPDI is coil coated on steel [249]. A coil coating primer for galvanized steel is made from polypropylene glycol and the reaction product from an epoxy resin, azelaic acid, and diethanolamine using CL blocked HDI and MF resin as cross-linkers [250]. A zinc-rich primer for steel uses an epoxy resin, a polyester resin, and a blocked isocyanate as binder [251]. Zinc-rich primers for coil coating application to galvanized steel that do not interfere with welding are based on blocked isocyanate and phenoxy resin [252] or a polyester, BPA epoxy resin, MEKO blocked HDI polyisocyanurate, and HMMM resin [253]. A primer which permits application of thick films without blistering is made from hydroxy-functional polyester, acrylic, and polybutadiene resins with DMP blocked HDI isocyanurate and an MF resin is patented for use under a fluorocarbon topcoat [254]. Ethyl acetoacetate blocked HDI biuret and an epoxy resin are used with non-chromate pigments to formulate a coil coating primer [255]. A corrosion protection primer for coil coating is formulated with blocked isocyanates and a polyester with anti-corrosion pigments [256]. Coil coating primer and topcoat formulations made with polyesters and CL blocked HDI isocyanurate have been patented [257]. An MEKO blocked IPDI adduct is used as a "flow modifier" to prevent edge pull away of a primer formulated with an acrylic resin and a poly(vinylidene fluoride) polymer [258].

A coil coating formulated with an ethylene imine blocked $H_{12}MDI$ triethylene glycol prepolymer with a hydroxy-functional polyester or acrylic resin has excellent flexibility and cures at 190°C in 30 s in contrast to the 60 s at 280°C required for a similar coating using HDI as a blocking agent [259]. An acetone oxime blocked IPDI isocyanurate/uretdione is formulated with hydroxy-functional polyesters [260]. An MEKO blocked mixture of TMXDI and $H_{12}MDI$ is used to cross-link a hydroxy-functional

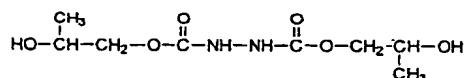
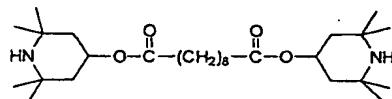
polyester [261]. An MEKO blocked HDI-terminated hydroxy-functional polyester is used with an epoxy resin to make a storage stable coating [262]. MEKO blocked $H_{12}MDI/TMP$ adduct, a hydroxy-terminated polyester, and the reaction product of BPA epoxy resin with DMAE and diisopropanolamine are suggested for use in coil coatings [263]. HDI isocyanurate blocked with diisopropylamine is reported to crystallize, use of diisopropylamine to block a combination of HDI isocyanurate with IPDI or $H_{12}MDI$ eliminates the crystallization problem; coil coatings cross-linked with such a combination exhibit superior gloss and less yellowing than when MEKO blocked HDI isocyanurate is used [264]. A coil coating is formulated with IPDI polyisocyanate, carboxylic acid- and hydroxy-functional polyester, glycidyl methacrylate acrylic resin, and decanedioic acid [265].

MEKO blocked HDI isocyanurate with a polyester is used in a white coating for galvanized steel [266]. A CL blocked mixture of IPDI and IPDI isocyanurate with a portion of the NCO groups left unblocked with hydroxy-functional polyesters gives a stable coil coating with a lower cure temperature [267]. A CL blocked IPDI isocyanurate prepolymer with 1-hydroxy-3-aminoethyl-3,3,5-trimethylcyclohexane has been patented for use in coil coatings [99]. Coatings are formulated with a hydroxy-terminated polyester and acetone oxime or CL blocked 1,5-diisocyanato-2-methylpentane and 1,4-diisocyanato-2-ethylbutane [268,269]. Clear coats are formulated with a hydroxy-functional resin and blocked isocyanate [270]. IPDI or HDI partially blocked with CL or MEKO made with a large excess of diisocyanate with the excess removed by vacuum thin film evaporation are said to be more compatible with polyesters than fully blocked ones. Presumably, the free NCO groups react with the hydroxyl groups of part of the polyester resulting in increased compatibility. Coatings made with HDI have much lower viscosities [271]. Blocked isocyanate coil coatings for galvanized steel are the subjects of a series of patents [272]. Coil coatings are formulated with IPDI uretdiones and hydroxy-functional polyesters with bismuth neododecanoate catalyst [273].

A coil coating for aluminum is based on MEKO blocked TDI-terminated polycaprolactone polyurethane, chlorinated rubber, and a phenol-formaldehyde resin [274]. MEKO blocked HDI polyisocyanate is used to cross-link an acrylic-polyester block copolymer for coil coatings [275].

A cross-linker for coil coatings with superior resistance to yellowing is made from HDI and IPDI isocyanurates, a hydrazine derived polyol and diisopropylamine as the blocking agent [276]. Yellowing can also be reduced by blocking HDI with a mixture of MEKO with small amounts of a hindered amine light stabilizer (HALS) with a free H on the N of the hindered amine and another small amount of the hydrazide obtained by reacting 1 mol of hydrazine with 2 mol of propylene carbonate [277]. To minimize yellowing 1,6-hexamethylene bis(*N,N*-dimethylsemicarbazide) is added to an MEKO blocked diisocyanate and polyester

polyol topcoat [278]. Coil coatings with excellent exterior durability and stain resistance are formulated with perfluoropolyether methyl ester diols and blocked isocyanate [279]. A blocked isocyanate fluoropolymer coating is formulated with a semicarbazide and an anti-oxidant to control yellowing during baking [280].



HALS/hydrazide anti yellowing combination

A waterborne coil coating is formulated with a hydroxy-functional cationic acrylic latex and a lactic acid modified IPDI blocked with dibutylamine and DMAE [20,281]. The cationic latex can also be designed to be self-cross-linking by using 2EH blocked IEM as a comonomer [281].

A coil coating primer that cures by a combination of UV curing and thermal curing is based on 2,6-di-*t*-butyl-4-methylphenol blocked H₁₂MDI/HEA adduct, a BPA epoxy resin, and benzoguanamine-formaldehyde resin [282].

Coil coatings that give striated surface textures are made with a hydroxy-terminated polyester, MEKO blocked HDI isocyanurate, and a thixotropic agent [283]. Clear films with a structured surface are obtained by coil coating a mixture of a hydroxy-functional acrylic resin, CL blocked IPDI, and powdered poly(methyl methacrylate) [284].

A coil coating resistant to growth of algae on the surface is formulated with a blocked isocyanate, an acrylic resin, and 2-methylthio-4,5-bis(ethylamino)-*S*-triazine [285].

A powder coil coating based on a combination of a hydroxyl and carboxylic acid-functional polyester, epoxy-functional acrylic, resin, and blocked isocyanate gives a coating with good hardness and flexibility, and improved weather resistance compared to coatings based solely on urethane or epoxy coatings [286]. A powder coil coating is formulated with a blocked isocyanate, a hydroxy-functional polyester, and an epoxy- and hydroxy-functional acrylate [287].

5.3. Electrodeposition coatings

By far the largest use of blocked isocyanates is in electrodeposition coatings (E-coats). Our searches revealed upward of 400 references, mostly patents, between 1980 and mid-2000. The largest share of E-coats is cationic E-coats and in turn the largest use of cationic E-coats is

for automotive primers. Almost all new cars and small trucks are primed with cationic E-coats; other large uses are primers or single coatings for trucks, appliances, agricultural implements, metal furniture and a wide variety of other manufactured products. In addition to this section, see Section 5.5 for E-coating wire and Section 10.2 for

E-coating printed circuit boards. Ref. [288] is an old but still useful review of cationic E-coats.

The vast majority of cationic E-coats are cross-linked with blocked isocyanates. These are used with hydroxy- and amine-functional resins as the principal binder. One example of such binder is illustrated in Fig. 9, which shows a water-dispersible derivative of BPA epoxy resin. In this system, the isocyanate reacts with the primary and secondary alcohols, as well as with residual amine. Many variations of epoxy derivatives are mentioned and described in the literature.

5.3.1. Isocyanates for E-coat

Half-blocked isocyanates such as the reaction product of equimolar amounts of 2,4-TDI and an alcohol such as 2EH followed by reacting the remaining NCO group with hydroxyl groups on a modified BPA epoxy resin (Fig. 10) can be used. The large difference in reactivity between the *para*- and *ortho*-isocyanates allows for the formation of predominantly mono-blocked product.

However, there is significant deblocking of both isocyanate groups during cure releasing some free TDI; this can migrate into base coats causing discoloration. The release of monomeric TDI can be suppressed by avoiding urethane linkages on both sides of the TDI. A patented method is to have the second NCO groups of a half-blocked TDI reacted with an aspartate ester; the resulting urea cyclizes to a thermally stable hydantoin upon heating (Fig. 11) [289]. Thus only one isocyanate group is released when the coating is baked. MDI isocyanurate blocked with a combination of CL and hexoxyethyl alcohol is also said to overcome the problem [290]. Another way to essentially eliminate the yellowing problem is to use CL blocked IPDI/TMP prepolymer as the cross-linker [291]. It is said that non-yellowing primers can be made with aromatic isocyanates by reacting

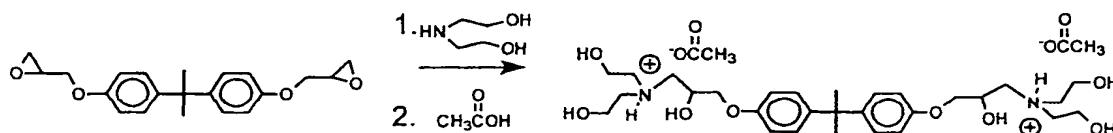


Fig. 9. Formation of water-dispersible BPA epoxy adduct.

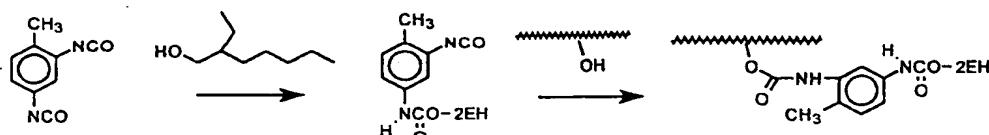


Fig. 10. Formation of half-blocked TDI-2EH adduct.

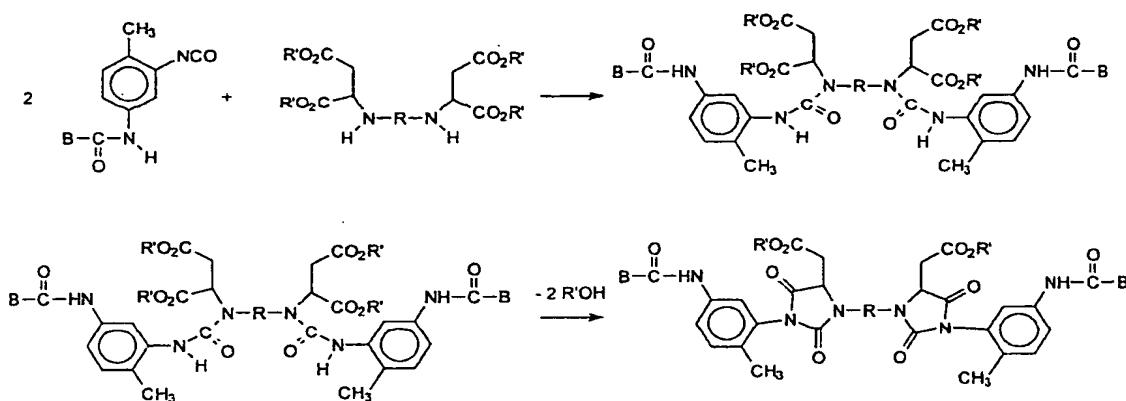
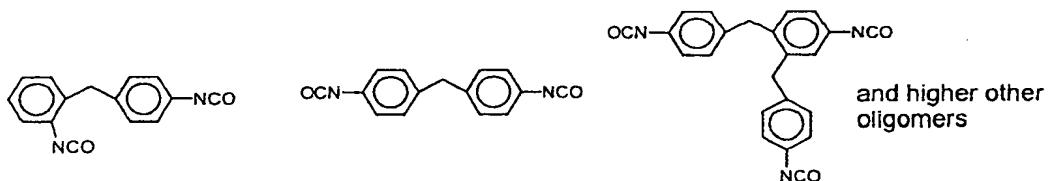


Fig. 11. Reaction of half-blocked TDI with an aspartate ester and cyclization of the product on heating.

TDI half-blocked by the butoxyethoxyethoxy alcohol with BPA epoxy to make an oxazolidone which is then used with a conventional modified epoxy resin [292]. In some cases, delamination on exterior exposure between the E-coat and topcoats has occurred, incorporation of HALS and a UV absorber in a 2-butoxyethoxyethyl alcohol blocked TDI primer has been reported to overcome this problem [293].

acid and dispersed in water gives a solvent-free cross-linker for E-coats [295]. Adhesion of topcoats to an E-coat primer is enhanced by incorporating some high NH-MF resin in the primer formulation having 2-butoxyethoxyethyl alcohol as a cross-linker; the melamine resin is said not to cure when the primer is baked but to react with hydroxyl groups in subsequent coatings enhancing adhesion [296].



Constituents of polymeric MDI

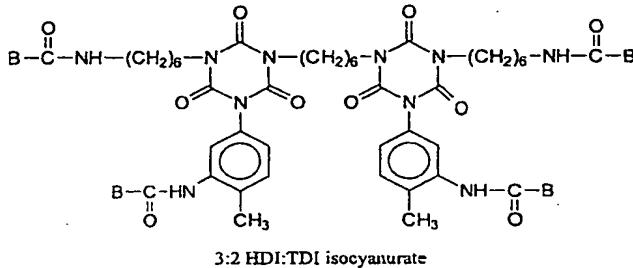
MDI and polymeric MDI have the advantage over TDI in that they are less mobile than TDI thus less likely to diffuse into base coats. E-coat dispersions are reported to be more stable using a polymeric MDI (12% 2,4'; 35% 4,4'; 53% poly) blocked with methyl alcohol (or other alcohols) [294]. Partially reacting the MDI with polyether polyols before blocking gives coatings with greater flexibility. A cationic PUD prepared from polymeric MDI partially blocked with 2-butoxyethoxyethyl alcohol, TMP, and *N,N*-dimethylaminopropylamine neutralized with formic

acid and dispersed in water gives a solvent-free cross-linker for E-coats [295]. Adhesion of topcoats to an E-coat primer is enhanced by incorporating some high NH-MF resin in the primer formulation having 2-butoxyethoxyethyl alcohol as a cross-linker; the melamine resin is said not to cure when the primer is baked but to react with hydroxyl groups in subsequent coatings enhancing adhesion [296].

A solvent-free E-coat is prepared by polymerizing a combination of partially 2EH blocked TDI, butyl glycol, TMP, and butyl methacrylate (or other acrylic esters) in the presence of a BPA epoxy-aminé resin [298].

A 3:2 HDI:TDI isocyanurate gives a non-yellowing formulation when it is blocked with a combination of CL and 2-ethylhexoxyethyl alcohol [299]. MEKO blocked

TDI/TMP prepolymer is used in an E-coat with improved crater resistance [300]. Another non-yellowing primer giving good resistance to delamination uses a combination of 2EH blocked MDI and MEKO blocked IPDI with a combination of epoxy–amine and hydroxy-functional acrylic resins [301].



While aromatic isocyanates have been used in most cationic E-coat primers, problems arise if UV radiation reaches the primer surface as a result of inadequate coverage by the base coat. Photodegradation can occur leading to discoloration and possibly delamination after outdoor exposure. Therefore, primers have been developed using aliphatic isocyanates; since aliphatic isocyanates deblock at higher temperatures than aromatic isocyanates, it is impractical to use alcohols as the blocking agent. A variety of other blocking agents has been used to achieve the desired lower baking temperature (see Section 5.3.2).

5.3.2. Blocking agents for E-coat

In recent years, as far as the blocked isocyanate component, primary focus has been on reducing the cure temperature by using other blocking agents and/or catalysts while maintaining the long term hydrolytic stability of the diluted coating. Since 2EH was the standard for many years, it is used as the base for comparison. Use of 2EH still continues as illustrated by a recent patent [302]. Patents also disclose the use of 2EH blocked TDI in the pigment grinding vehicle even though the main cross-linker is blocked with some other blocking agent, e.g. see Refs. [303,304]. Phenols give lower cross-linking temperatures and have been investigated [305]; however, at least in most cases, they are not practical due to emission of phenols from the baking ovens. *p*-Chlorothiophenol has been reported to have an especially low deblocking temperature [182].

A variety of lower molecular weight alcohols have been recommended to reduce curing temperatures including: methyl alcohol [294,306], ethyl alcohol [294,306], isopropyl alcohol [307], sec-butyl alcohol [308], *n*-butyl alcohol [309], and furfuryl alcohol [310]. Use of a mixture of methyl and ethyl alcohols for blocking an MDI/TMP prepolymer cross-linked E-coat is said to improve surface leveling over rough steel as compared with 2EH; the decreased volume shrinkage due to the lower molecular weight alcohols is proposed as a reason for the improvement [311]. A high throw power E-coat is formulated with

tridecyl alcohol blocked prepolymer of polymeric MDI with 2,2,4-trimethylpentane-1,3-diol and TMP with an epoxy–amine resin compound [312].

Several monoethers of ethylene glycol and diethylene glycol have been used:

- 2-ethoxyethyl alcohol [313];
- *n*-propoxyethyl alcohol [314];
- methoxypropyl alcohol [315];
- 2-butoxyethyl alcohol [294,316];
- 2-butoxyethyl alcohol blocked TDI/TMP phenoxypropyl prepolymer [317];
- 2-ethylhexoxyethyl alcohol [318];
- 2-ethoxyethoxyethyl alcohol [319];
- 2-ethoxybutoxyethyl alcohol [320];
- butoxyethoxyethyl alcohol [292,321–324];
- mixed CL and hexoxyethyl alcohol [290] have been patented;
- combinations of methyl alcohol, ethyl alcohol, and butoxyethoxyethyl alcohol [325,326];
- β -hydroxyurethanes such as that made by blocking a TDI/TMP prepolymer with hydrolyzed butylglycidyl ether [327].

Presumably, these ether alcohol blocked isocyanates cross-link at lower temperatures than those blocked with alkyl alcohols since the reverse reaction to reform the blocked isocyanates is slower than with alcohols (see Section 2.2.1). It is also possible that due to their low volatility the glycol ethers remain in the film longer promoting better flow and leveling. We have not found a systematic comparison of these various glycol ether blocking agent, clearly there are differences in cure responses. For example, it is reported that methoxypropyl alcohol is “sluggish” compared with 2-butoxyethoxyethyl alcohol [303].

Lower cure temperature E-coats are formulated with monoethers of resorcinol and glycols, such as 2-(2-hydroxyethoxy)phenol, with a polyisocyanate such as polymeric MDI [304,328].

A combination of 2EH blocked TDI and 2-butoxyethyl alcohol blocked triisocyanate is used with epoxy/amine binders and hydroxy-terminated acrylonitrile/butadiene copolymer [329]. 2-Ethoxyethyl alcohol blocked TDI/[4-(HOCH₂CH₂)₂CHCOOH] prepolymer in epoxy E-coats; the COOH group also reacts with an epoxy group [330]. BPA can be reacted in making the epoxy resin to leave some terminal phenol groups; when used in an E-coat primer along with butoxyethoxyethoxyethyl alcohol blocked polymeric MDI, E-coat primers can be made that do not require lead in the formula nor require chromic acid wash of phosphate conversion coatings [331].

Glycol amides such as *N,N*-dibutylglycolamide have been patented as a blocking agent permitting lower temperature cure in E-coats as compared with 2EH [332]. 2-(Hydroxymethyl)pyridine has been patented as a blocking agent for use in cationic E-coats; it is said to give more rapid cure than *N,N*-dibutylglycolamide or furfuryl alcohol

and equal cure to that with 2-heptanone oxime and DMP and greater stability in the presence of amines than the latter two [333]. DMAE has been used as a blocking agent for TDI in primers [334].

MEKO blocked TDI isocyanurate is reported to give primers that cure in 20 min at 120°C compared to 20 min at 170°C required for a primer with CL blocked TDI [335] or 2EH blocked XDI [336]. MEKO blocked TDI polypropylene glycol prepolymer has been patented for E-coats [337]. MEKO half-blocked TDI is reacted with an aminophenol modified epoxy resin [338]. A graft copolymer of MEKO blocked IEM, styrene, DMAE methacrylate, and BPA epoxy resin has been patented for use in E-coat primers [339]. An acrylic/epoxy E-coat uses MEKO blocked IPDI as the cross-linker [340]. MEKO blocked HDI/TMP prepolymer is used as a cross-linking in an E-coat primer for galvanized steel [341]. While MEKO provides lower cure temperatures, it has been shown that in the E-coat process, HCN is generated leading to dangerous waste discharges [342]. Use of methyl amyl ketone oxime to block a TDI/TMP prepolymer with an epoxy–amine resin and a cationic hydroxy-functional acrylic resin gives E-coats with better leveling than when MEKO is used [343].

Use of a water-dispersible blocked isocyanate prepared from butoxyethoxyethyl alcohol blocked oligomeric MDI, TMP, and *N,N*-dimethylaminopropylamine neutralized with formic acid has been patented [295].

Microgel particles made with a BPA epoxy amine derivative and an oxime blocked isocyanate have been patented as additives to E-coat primers [344]. Primers that retain good edge covering in the baking oven are prepared by adding a dispersion of gelled particles of an epoxy–amine polymer cross-linked with MEKO blocked TDI [345]. A large variety of microparticles have been patented to control edge flow of E-coats, e.g., an aqueous dispersion of a diethylamine salt of a maleic anhydride adduct of polybutadiene particles, was used with an epoxy–amine and 2EH blocked TDI [346]. Gel particles from acrylic copolymers also improve edge coverage [347]. Use of a mixture of MEKO blocked TDI and IPDI gives a primer with a combination of low and high temperature deblocking which minimizes creeping away from edges during baking [348]. Better edge coverage is also claimed for incorporation of a water thickener, hydroxyethylcellulose, in an E-coat such as one prepared with di-*n*-butylamine blocked HDI isocyanurate and an epoxy–amine product [349].

Improved leveling is reported using a butadiene, styrene, HEMA latex along with an epoxy–amine and butoxyethoxyethyl alcohol blocked polymeric MDI/TMP prepolymer [324]. Improved leveling with a reduction in cratering, is reported using an acetic acid salt of a polyurethane made with HDI, a polyether diol, and the methyl isobutyl ketone (MIBK) ketimine of DETA as an additive to a cationic electrodeposition bath [350]. The additive cross-links with the main binder of the E-coat. Another additive is said to reduce cratering is the reaction product of glycidyloxypropyltrialkoxysilane with a polyoxyalkylene-

diamine [351]. Use of CL [352], benzyltriazole [353] and di-*n*-butylamine [354] has been patented. Diallylamine blocked MDI [355] and dimethylamine blocked TDI [356] are said to cure faster than 2EH blocked isocyanates in E-coats. The MIBK ketimine of methylaminopropylamine has been used as a blocking agent for TDI polyester polyol prepolymer with cross-linked micro-resin particles and an epoxy derivative to make an E-coat that gives superior edge coverage [357]. Chip resistant E-coat primers have been made using TDI polyglycol prepolymer blocked with dibutylamine [358]. TDI blocked with 2-*N*-methylaminoethyl alcohol has been reported to give primers curing in 30 min at 140°C [359]. TDI blocked with an enamine derivative of acetylacetone permits curing at temperatures as low as 120°C [360]. Use of DEM blocked TDI in low temperature curing primers has been claimed [361]. The use of TDI half-blocked with TMP ethyl malonate and half with methoxyethyl alcohol has been patented [362]. Use of DMP blocked TDI prepolymer with TMP and diethylene glycol has been patented [363].

When it is necessary to use aliphatic isocyanates for UV stability, a variety of such isocyanates have been used with blocking agents that permit sufficiently low temperature curing. 2-Ethoxyethyl alcohol blocked HDI [364] and 2-butoxyethyl alcohol blocked IPDI pigmented primers [365] and the latter in a pigment-free primer [366]. Use of DMP blocked IPDI prepolymer [367] and H₁₂MDI [368] have been patented. *t*-Butyl acetoacetate blocked HDI has been used [368]. Copolymers CL blocked vinyl isocyanate [369] or cyclohexyl alcohol blocked vinyl isocyanate [370] with *N*-[3-(dimethylamino)propyl]methacrylamide and an acrylic ester with a BPA epoxy adduct with DMAE have been patented as binders for E-coats. Use of MEKO blocked HDI isocyanurate [371,372], MEKO blocked HDI dimer [373], and MEKO blocked IPDI [374] have also been patented. A combination of 2-ethylhexoxyethyl alcohol blocked MDI and MEKO blocked IPDI is recommended [375]. MEKO blocked XDI/TMP prepolymer is used in a primer that cures at 170°C [376]. MEKO blocked HDI or IPDI prepolymers with TMP-based primers are said to cure at 160°C [377]. MEKO blocked IPDI and mixed TDI and IPDI blocked with a combination of 2EH and DMAE-based primers are reported to cure at 150°C compared with 180°C for a mixed TDI and IPDI blocked with 2EH [378]. Curing temperatures are reported to be lower when MEKO blocked HDI isocyanurate is used when the average functionality of the isocyanurate is high, with average number of NCO groups of 5.1–7.6, and including *N,N*'-dimethylhydrazide groups to minimize yellowing [379]. Use of MEKO blocked 2,5(6)-bis(isocyanatomethyl)bicyclo[2.2.1]heptane (norbornane diisocyanate) has been patented [380]. MEKO blocked HDI has been used in an E-coat said to have superior leveling [381]. MEKO blocked XDI prepolymer with polypropylene glycol-modified polybutadiene and an epoxy resin are used in an impact resistant primer [382]. TMXDI partially reacted with HEMA and MEKO is copolymerized

with styrene to give a low molecular weight polymer that is used as a cross-linker [383]. MEKO blocked TMXDI/TMP prepolymer permits curing at 120°C, compared to 165°C with 2EH blocked TDI [384]. Mixtures of methyl alcohol, ethyl alcohol, and 2(2-butoxyethoxy)ethyl alcohol or methyl alcohol and 2-hexoxyethyl alcohol have been used to block TMXDI/TMP prepolymer [385]. 2EH blocked 1,3,5-trisocyanato-S-triazine has been patented as a cross-linker [386]. Glycol ether blocked isocyanates prepared by reacting HMMM resins with glycol monoethers (see Addendum, Section 3.2) can be used in formulating E-coats [387].

Di-*n*-butylamine has been used to block H₁₂MDI [388], HDI isocyanurate [389,390], HDI [391], and IPDI ethoxylated TMP/BPA prepolymer [392]. It is reported that when *n*-butylamine blocked HDI isocyanurate is used as a cross-linker no further catalyst is required [393]. IPDI blocked with a mixture of MEKO and dimethylaminopropylamine cross-linked primer can be baked at 120°C [394]. DEM blocked HDI isocyanurate is said to give primer that cures in 20 min at 130°C compared to 170°C for a CL blocked TDI coating [395]. 2-Ethoxyethyl alcohol and a transesterification product of DEM and TMP are used to block TDI, thus cure results from two different mechanisms [396]. A formulation using a combination of an epoxy–amine resin and a carboxylic acid-functional acrylic resin with CL blocked IPDI/TMP is said to cross-link both by urea–urethane formation by the isocyanate and transesterification reactions by the carboxylic acid groups [397].

Another approach to improving exterior durability is to use an amine-modified epoxy resin with a non-ionic hydroxy-functional acrylic latex and a combination of MDI blocked with 2-ethylhexoxyethyl alcohol and IPDI blocked with MEKO [398]. Gel particles made by reacting *n*-propyl alcohol blocked TDI adduct of hydroxypropyl methacrylate and DMAE with peroxide initiator and then dispersing in acidic water used in an *di-n*-butylamine blocked HDI isocyanurate containing E-coat primer to improve edge coverage [390].

One of the requirements for satisfactory application of E-coats is to maintain the temperature of the bath within a narrow range to assure consistent film builds. Higher temperatures permit better flow and use of lower voltages. A patent has been issued that is said to minimize the need for temperature control by using a combination of two blocked isocyanate compounds with T_g 's that differ by at least 25°C [399]. This is said to permit coalescence over a wider range of temperatures. One of several such pairs investigated was a blocked compound made with a mixture of CL and hexoxyethyl alcohol with MDI isocyanurate ($T_g = 31^\circ\text{C}$) and MEKO blocked HDI isocyanurate ($T_g = -14^\circ\text{C}$).

A group of patents claims significant advantages in using for an E-coated primer, a formulation that can then also be sprayed over the primer and over plastics on the assembled car body such as polycarbonates and polyesters to give the required adhesion [400]. For example, use of an MEKO

blocked HDI, epoxy–amine resin, and a reaction product of hydrogenated styrene/butadiene resin reacted with maleic anhydride is patented.

By using 1,2-bis(isocyanatophenoxy)ethane TMP prepolymer instead of MDI in making the binder, more flexible films are obtained, the methoxyethoxyethoxyethyl alcohol is used as the blocking agent [401]. Addition of hydroxy ethylethylene urea as a reactive diluent, is said to improve flow, reduce required curing temperature, and increase chip resistance of 2EH blocked TDI E-coat primers; presumably the reactive diluent reacts with isocyanate after it is released in baking [402]. A chip resistant primer with good throwing power is formulated with butoxyethyl alcohol blocked MDI propylene glycol prepolymer with a hydroxy-functional polyester in addition to the epoxy–amine resin [403]. Addition of a hydroxy-functional polyurethane with the epoxy–amine and using propoxyethyl alcohol blocked TDI/TMP prepolymer gives coatings with improved leveling and chip resistance [404]. 2EH blocked TDI/TMP butylene glycol prepolymer adduct of HEMA has been added to E-coat primers [405]. Incorporation of a formal of butoxyethoxyethyl alcohol in an E-coat based on epoxy resin and 2EH blocked TDI improves the smoothness of E-coated primers [406]. Improved flow can be obtained by reacting TDI blocked with a mixture of methyl alcohol and 2-ethylhexoxyethyl alcohol with a propoxylated BPA and in turn reacting this with a BPA epoxy resin before making an amine derivative [372].

While most cationic E-coat primers are based on amine-modified epoxy resins, some use other base resins. BPA epoxy resin is reacted with adipic acid and DMPA to give a hydroxy-terminated resin where all the epoxy groups have been reacted. It is in turn reacted with IPDI and DETA/MIBK ketimine to yield an amine-terminated polymer that is acidified and mixed with 2EH half-blocked TDI to give an E-coating [407]. A cationic E-coat is based on an acrylic copolymer of CL blocked vinyl isocyanate, styrene, butyl acrylate, 2-hydroxylpropyl methacrylate, and *N,N*-diethylaminopropyl methacrylamide [408]. Cationic E-coats have been formulated with acrylic resins and blocked isocyanates [409]. Another non-yellowing cationic E-coating is formulated with a hydroxy-functional, epoxy-functional acrylic resin reacted with diethylamine to make it acid dispersible, another hydroxy-functional acrylic resin whose hydroxyl groups are reacted with CL half-blocked HDI, and a CL blocked IPDI/TMP prepolymer [410].

An E-coat primer is formulated with a mixture of two aqueous dispersions, one of a conventional epoxy–amine resin with methyl alcohol, ethyl alcohol, and butoxyethoxyethyl alcohol and the other, an aqueous dispersion of an acrylic resin made with DMAE methacrylate and HEA as comonomers with MEKO blocked MDI [411]. An emulsion of a hydroxy-functional acrylic resin stabilized with a dispersing agent made from dimethylaminopropylamine blocked polymeric MDI butoxyethoxyethyl alcohol, butylene glycol, TMP prepolymer is added to an epoxy–amine

binder for E-coat primers [412]. Phenol-modified cyclized rubber, a polybutadiene oil, an amine-terminated polyamide, and with a mixture of TDI half-blocked with DMAE and TDI half-blocked with ethoxyethyl alcohol has been patented as a binder for cationic E-coats [413]. Use of a diallylamine blocked TDI prepolymer with hydroxy-functional amine-terminated polyamides has been patented [414].

A conductive E-coat primer is formulated using 2EH blocked TDI with an epoxy–amine resin and electroconductive black pigment [415]. A conductive E-coat primer that can be topcoated with another E-coat is formulated with an acrylic resin made with DMAE methacrylate, HEA, and hydroxypropyl acrylate as comonomers, CL blocked HDI biuret, and conductive carbon black pigment [416]. Another conductive E-coat primer is made with graphite and zinc powder [417]. A light colored conductive E-coat primer double coated to give good edge coverage is formulated with butoxyethoxyethyl alcohol blocked TDI with antimony containing tin oxide coated on SiO_2 [418]. A multiple coat system is made with a conductive E-coat primer, baked and then electrocoated with a pigmented base and finally spray topcoated with a clear finish [419]. A multiple coat system is made by first E-coating with a conductive primer formulated with butoxyethoxyethyl alcohol blocked TDI with antimony containing tin oxide, then coating with a pigmented conductive primer–surfacers, and finally E-coating with cationic acrylic, blocked isocyanate clear gloss topcoat [420]. A wet-on-wet three coat system uses a primer formulated with an epoxy–amine dispersion, dibutylamine blocked HDI isocyanurate; after electrocoating, the coated article is rinsed. It is then electrocoated with a color pigmented second coat formulated with a cationic water-reducible hydroxy-functional acrylic resin and an MEKO blocked polyfunctional isocyanate based on HDI and the coated article is rinsed. A third coating, a clear or aluminum pigmented topcoat, with a similar binder system is applied by electrodeposition and the coated article baked [421].

While primer is the major use of cationic E-coat, topcoats can also be made. E-coats for aluminum are formulated with MEKO blocked HDI isocyanurate and an acrylic copolymer of butyl acrylate, MMA, styrene, HEMA, dimethylaminopropylacrylamide and *N*-butoxymethylacrylamide neutralized with lactic acid [422]. A white topcoat is formulated with CL blocked IPDI/TMP and a cationic acrylic resin made by reacting diethylamine with a hydroxy-functional acrylic resin made using glycidyl methacrylate as a comonomer [423]. A copolymer from acetone oxime half-blocked HDI adduct with glycerol reacted with HEMA with acrylic esters including DMAE methacrylate is applied by E-coat and baked for 20 min at 140°C [424]. Use of benzyl methacrylohydroxamates blocked MDI copolymerized with acrylic copolymers of DMAE methacrylate, HEA, methacrylamidopropyl(2-hydroxyethyl)dimethylammonium acetate, and other monomers for E-coats has been patented [425]. CL blocked TMI copolymerized with DMAE methacrylate, HEA and other monomers, then with an epoxy

resin has been used as a binder for E-coat [426]. A water-borne 1K clear coat is formulated with a graft copolymer from an MEKO blocked TMI hydroxy-functional acrylic resin grafted with another acrylic made from HEA and dimethylaminopropyl methacrylate neutralized with acetic acid [70]. 2EH blocked [427] and MEKO blocked [428] IEM have been used to make acrylic resins using HEMA and DMAE methacrylate as comonomers. A hydroxy-functional cationic acrylic latex and a hydroxy-functional water-reducible acrylic resin have been used with an MEKO blocked IPDI adduct [428]. CL blocked TDI-terminated cationic PUDs have been made from propoxylated BPA, polyethylene glycol, propoxylated TMP, TDI, CL, and *N,N*-bis(2-hydroxyethyl)-2-aminoethyl nitrile [429]. Cationic latex for E-coat has been patented adding an emulsion of a CL blocked IPDI adduct during the emulsion polymerization of an acrylic latex with hydroxypropyl methacrylate and DMAE methacrylate as comonomers [430].

5.3.3. Catalysis

Considerable effort has been devoted to development of new catalysts for E-coatings. There have been three driving forces: preparation of lead-free primers, reduction of curing temperatures and increased hydrolytic stability. Dibutyltin oxide has been most commonly used catalyst; it gives good stability, but it is a pigment and must be dispersed with the other pigments and is not highly efficient and generally requires a lead compound as a cocatalyst. Lead cyanamide is said to be an effective supplementary catalyst with dibutyltin oxide [431]. DBTDL has insufficient bath stability, dibutyltin esters with more hydrophobic groups such as dibutyltin dioleate and dibenzoates give better bath stability and cure [432]. Dialkyltin dibenzoates are also said to have better bath stability than DBTDL or dialkyltin oxides [433]. Use of a combination of dibutyltin dibenzoate with zirconium or bismuth hydroxide as catalysts for 2-ethoxyethyl alcohol blocked TDI decreases cure temperature and improves corrosion resistance with lead compounds in the E-coat [434]. Tetrabutylstannoxane diesters, such as benzoates, have been patented as showing good compatibility and bath stability [433,435]. Addition of abietic acid to a DBTDL catalyzed 2-(2-butoxyethoxy)ethanol and 2-butoxyethanol blocked oligomeric MDI containing E-coat primer reduces curing temperature [436]. This may be due to the exchange of the laurate groups with the abietic acid. When used with enfoliated clay pigment, this blocked isocyanate cross-linked coating gives improved cratering resistance [437].

A large number of trialkyltin oxides, triphenyltin oxide and bis(trialkyltin) oxides have been evaluated as catalysts, all gave much faster cure than dibutyltin oxide [438]. Trialkyltin compounds such as bis(trioctyltin) oxide (TOTO) are said to be particularly effective catalysts especially when used along with ZnO [439]. A series of patents discusses various possible catalysts and particularly recommends TOTO that permits curing at 150°C [440]. It is claimed that

with TOTO one can obtain thicker coatings, greater throw power, and better edge coverage. TOTO is low in toxicity and is a liquid that is easily incorporated into the coating, and can be used to make clear coatings. Bis(tributyltin) oxide is reported to be a more efficient catalyst and more easily incorporated than dibutyltin oxide [441]. Reaction products of dibutyltin oxide with a variety of hydroxy acids such as 4-hydroxyphenylacetic acid, and dibutyltin oxide 2,3-dihydroxypropyl mercaptide are effective catalysts for E-coat, hydrolytic stability of the mercaptide is especially good [442]. 2,2-Dibutyltin-1,3-oxathiacyclohexan-5-ol [443] and polymers made by reacting dibutyltin oxide with 3-mercaptopropanediol [444] are reported to provide excellent stability and catalytic activity. Reaction products of dibutyltin oxide and polyphenols, such as BPA, are reported to be effective catalysts [315,445]. Dibutyltin diacetone has been patented as a hydrolytically stable catalyst [446]. Metal complexes of dibutyltin diacetatoacetone with such metals as tin and cobalt have been patented [447].

Addition of a fatty acid, such as oleic acid, is reported to enhance the catalytic activity of dibutyl tin oxide and DBTDL [303]. Addition of hydroxamic acid to a cationic E-coat primer is reported to reduce catalyst concentration required and enhance corrosion resistance [448].

Bismuth salts have been reported to be particularly effective catalysts. For example, use of the salt obtained by reacting an amino acid such as alanine with Bi_2O_3 , especially when a small excess of the amino acid is used in making the salt has been patented [449]. The adduct of dibismuth trioxide with DMPA and converted to a salt during emulsification into an epoxy–amine binder is reported to be a good catalyst [450]. Bismuth salts of lactic acid and with DMPA are reported to be effective catalysts having the advantage that the phosphate conversion coating does not need a chromate wash when they are used as catalysts for the E-coat primer [451]. A mixture of bismuth lactate and bismuth lactate is patented to use as an E-coat catalyst [452]. The effectiveness of a series of catalysts on the cure of a cationic E-coat in which 2-butoxy-2-ethoxyethyl alcohol blocked polymeric MDI was the cross-linker concluded that a bismuth salt, such as bismuth tris(isostearate), plus a carboxylic acid, such as isostearic acid, gave the best cure response as well as superior resistance to hydrolysis [453]. Bi_2O_3 and its derivatives are reported to be superior catalysts to BiO_2 [326]. Bismuth salts of hydroxy acids, such as DMPA, are reported to be good catalysts with TDI half-blocked with TMP ethyl malonate and half with methoxyethyl alcohol [362]. However, [449] says that bismuth hydroxy acid salts are prone to hydrolysis, making the E-coat bath more corrosive and yielding bismuth oxide that is insoluble and a relatively ineffective catalyst. Bismuth compounds, such as bismuth dimethyldithiocarbamate, are reported to be excellent catalysts [328]. The corresponding zinc compound is reported to be a slightly better catalyst but bath stability is poorer, bath odor is offensive, and coated films show more defects.

Ferric octanoate has also been recommended as a catalyst

for E-coats [454]. Salts of various metals with organic acids, preferably water-soluble salts, together with organotin compounds are effective catalysts [455]. The reaction product of $\text{Fe}(\text{AcAc})_3$, salicylaldehyde, and 1,2-dimethylimidazole, with di-n-butylamine blocked HDI isocyanurate gives primers that cure at 160°C [389]. Methyltriethylammonium formate has been patented for use with 2-butoxyethyl alcohol blocked TDI [456].

5.3.4. Anionic E-coat

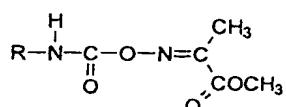
Anionic E-coats using blocked isocyanates have been the subject of very few patents. IPDI blocked 12-hydroxystearic acid has been patented for use with anionic epoxy–amine E-coats [457]. CL blocked HDI biuret has been formulated with a carboxylic acid-functional polyester, the reaction product of a BPA epoxy resin with 2-butoxyethyl alcohol, and a hydroxy-functional polyester with diisopropylamine [458]. Phenol blocked TDI [459] and a phenol blocked HDI/THEIC [460] have been used with COOH- and OH-functional water-reducible acrylics for anionic E-coats. t-Butyl alcohol blocked vinyl isocyanate copolymerized with hydroxypropyl acrylate, acrylic acid, and other monomers is used to prepare self-cross-linking water-reducible acrylic polymers [461]. Cyclohexyl alcohol blocked vinyl isocyanate, butyl acrylate, and acrylic acid copolymerized with an adduct of a BPA epoxy resin and allyl alcohol neutralized with DMAE is used for anionic E-coating [462]. An E-coating having superior color properties is reported to be made with CL blocked IPDI/TMP with a polyester prepared from the glycidyl ester of versatic acid and trimellitic anhydride [463].

5.4. Automotive coatings

5.4.1. Topcoats

Oxime blocked isocyanates, particularly using MEKO, are widely used for cross-linking hydroxy-functional resins. For example, MEKO blocked H_{12}MDI [464] and TMXDI [465] with a combination of hydroxy-functional acrylic and polyester resins give etch resistant clear topcoats that can be cured at 150°C. However, MEKO blocking agent cured coatings tend to yellow during curing and exposure. The problem is particularly severe in the case of clear coats over acid-catalyzed MF acrylic white automotive base coats [466]. Yellowing can be reduced by replacing the dodecylbenzenesulfonic acid and high HMMM resin in the base coat with high NH-MF resin [467]. Although ketoximes based on hindered ketones cure at lower temperatures than MEKO, yellowing is worse, presumably because they do not volatilize as rapidly as MEKO. Clear coats cross-linked with a combination of MF resins and MEKO blocked isocyanate yellow less than without the MF resins [468]. Isocyanates blocked with methyl pyruvate oxime are reported to have low unblocking temperatures and to be non-yellowing [469]. Clear coats have been formulated with an epoxy-functional, hydroxy-functional acrylic resin, an

oligomeric hydroxy-functional polyester, MEKO blocked IPDI isocyanurate and MF resins [470]. Clear coats that cure in 30 min at 130°C have been formulated with MEKO blocked HDI isocyanurate and a combination of sterically hindered amine oligomers, one made from maleic anhydride, 1,6-hexanediol, polyethylene glycol, and IPDA, the other with TMP triacrylate and IPDA [471]. An MEKO blocked mixture of HDI and IPDI and MF resin are used to cross-link a combination of a coreactant obtained by reacting citric acid with glycidyl neodecanoate then with methyl carbamate and the product of reacting hydroxypropyl carbamate with caprolactone to give a clear coat [472].

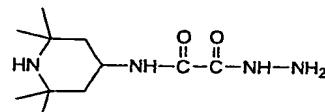


Methyl pyruvate oxime blocked isocyanate

A long list of anti-oxidants was tested for their affect on yellowing, best results were obtained with *N*-2,2,6,6-tetramethyl-4-piperidinyl-*N*-amino oxamide and the hydrazide made by reacting hydrazine hydrate with propylene carbonate; they were used in making MEKO blocked HDI isocyanurate prepolymers [473]. Addition of hydrazide derivatives has also been found to reduce yellowing (Fig. 12) [474]. MEKO blocked IPDI adduct of TMP and *N*-amino hydroxyisopropylcarbamate (made by reacting propylene carbonate with hydrazine in ethyl alcohol) is used with MEKO blocked HDI and MEKO blocked IPDI to reduce yellowing [475].

MEKO blocked HDI isocyanurate with a hydroxy-functional acrylic resin that includes cyclohexyl methacrylate as one of the comonomers and incorporating an HALS and UV absorber in the formulation gives a clear coat with excellent environmental etch and mar resistance with reduced yellowing [476]. Inclusion of silane-treated silica sol in a clear acrylic topcoat cross-linked with MEKO blocked HDI isocyanurate gives a surface with excellent stain resistance [477]. Yellowing can also be reduced by blocking HDI with a mixture of MEKO with small amounts of HALS with a free H on the N of the hindered amine and a small amount of the hydrazide obtained by reacting 1 mol of hydrazine with 2 mol of propylene carbonate [277]. HDI isocyanurate

(and others) blocked with a mixture of MEKO and a HALS derivative with a hydrazide substituent have been used [478].



Hydrazide-functional HALS

Another concern with oxime blocked isocyanates is toxic hazard; oximes, in general, are considered toxic hazards especially at elevated temperatures [479].

The combination of underbake performance and, for some applications, yellowing, has led to use of alternative blocking agents such as pyrazoles and triazines. Acrylic coatings made with isocyanates blocked with DMP cure more rapidly than when MEKO is used and yellowing is less [480–482]. 1,2,4-Triazole blocked isocyanates are intermediate in cure rate and give still less yellowing than DMP [481]. The use of mixtures of DMP and triazole has been recommended as blocking agents for automotive clear coats; the combination gives almost as fast curing as DMP alone and almost as good resistance to yellowing as triazole alone [481]. DMP is more expensive than triazole but triazole blocked isocyanates tend to crystallize out of a coating. Use of 3,5-dimethyl-1,2,4-triazole instead of 1,2,4-triazole gives blocked HDI or IPDI derivatives that have lower viscosity and do not crystallize; when formulated with a hydroxy-functional acrylic resin clear topcoats are obtained that cure in 30 min at 140°C [483]. HDI (or isophorone diisocyanate (IPDI)) blocked with a combination of DMP and 1,2,4-triazole with a mixture of hydroxy-functional acrylic and polyester resins shows little yellowing and no crystallization [484]. A mixture of DMP blocked IPDI, DMP blocked HDI and MF resin is used to cross-link a carbamate- and hydroxyl-functional acrylic resin to give clear coats with improved yellowing resistance [485]. The flow properties of the coating after application are said to be superior with the combination of cross-linkers, the inventors propose that the MF resin reacts first with the carbamate groups building the viscosity of the coating controlling sagging, then after the coating levels the hydroxyl groups react with the freed isocyanate groups to provide the final cross-linking.

Ethyl acetoacetate blocked IPDI isocyanurate made with sodium methoxide catalyst and then neutralized

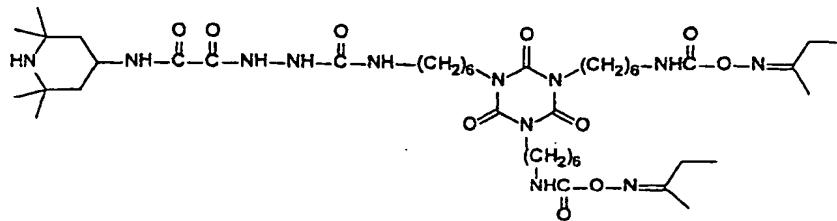


Fig. 12. A hydrazide derivative of MEKO blocked HDI isocyanurate.

with di-2-ethylhexyl phosphate has been patented for non-yellowing topcoats [486]. DEM blocked isocyanates are used with hydroxy-functional polyesters to make base coats and clear topcoats with reduced yellowing [487]. Addition of a small amount of *p*-formaldehyde to the reactor after making DEM blocked isocyanurates reduces yellowing [488]. A stable, colorless HDI isocyanurate blocked with a combination of DEM and 1,2,4-triazole with *p*-formaldehyde is used as a cross-linker [489]. A combination of DEM and ethyl acetoacetate blocked HDI isocyanurate is used with a hydroxy-functional acrylic resin for clear coats [490]. DEM blocked IEM acrylic copolymers with a hydroxy-functional acrylic are used as the binders in a 'IK coating [491]. A combination of DEM blocked IPDI and MF resin are used for cross-linking hydroxy-functional acrylic resin clear coats [492]. DEM blocked IPDI trimer and MF resin are used as cross-linkers for a hydroxy-functional acrylic resin polymerized in a solution of a hydroxy-functional polyester resin to formulate a clear topcoat [493]. DEM blocked isocyanates have the advantage of combining low temperature cure with good package stability when formulated with a monoalcohol such as isopropyl alcohol (see also Section 3.8) [494].

Use of glycol ether blocked isocyanates prepared by reacting glycol ether carbamates with HMMM resins to cross-link hydroxy-functional [387] and acetoacetoxy-functional [495] acrylic resins in formulating clear coats. Alcohol and glycol blocked isocyanates prepared by reacting HMMM with propyl carbamate and hydroxypropyl carbamate, respectively, are used to cross-link hydroxy-functional acrylic resins [496].

The reaction products and kinetics of the reactions occurring when acrylic resins are cured with both MF resins and CL blocked MDI have been studied [497]. In the case of unblocked MDI with only HMMM resin, there is a reaction of the isocyanate groups through the carbocation formed by splitting within the methoxymethyl groups. With a polyether polyol included in the combination, the only reactions detected were methoxymethyl groups reacting with hydroxyl groups and isocyanate reacting with the methoxymethyl groups but no reaction of isocyanate with polyol hydroxyl groups. This latter observation was attributed to the more rapid reaction of isocyanate with the methyl alcohol released than with the polyol hydroxyl groups. When CL blocked MDI was used, there was cross-linking of the polyol hydroxyl groups with isocyanate as well as with

the MF resin and reaction of the MF resin with the polyol hydroxyl groups but the cure temperature was higher due to the slower rate of freeing the isocyanate groups.

Malonic ester blocked isocyanates react with MF resins [498]. Studies of the reaction of a model compound, DEM blocked with butyl isocyanate with high HMMM resin catalyzed with *p*-toluenesulfonic acid showed that the hydrogen on the blocked isocyanate disappeared. Since the reaction could be carried out without interference in a methanol solution, the reaction is not reversible, indicating formation of a carbon–carbon bond (Fig. 13). Malonic ester blocked HDI was used with MF resin as a co-cross-linker for acrylic polyols; the cure rate was comparable to MF resin alone. The reactions are complex; the MF resin reacts with hydroxyl groups on the acrylic and also with the active methine group of the malonic ester derivative and also the malonic ester derivative reacts with the hydroxyl groups of the acrylic. The result is a clear topcoat that combines environmental etch resistance and mar resistance. A reduced yellowing binder for pigmented coatings is formulated with a combined DEM and ethyl acetoacetate blocked HDI isocyanurate, MF resin, and a hydroxy-functional acrylic resin [499]. Ethyl acetoacetate blocked HDI biuret and MF resin are used to cross-link hydroxy-functional acrylic and polyester resins for use in clear topcoats [500].

TACT (see Section 2.3) can be used as a cross-linker for hydroxy-functional acrylics giving coatings better in environmental etch resistance and accelerated exterior exposure resistance than MF resins, approaching those obtained with IPDI cross-linking [501,502]. Properties are better when HEA is the comonomer used in making the acrylic resin than when HEMA is used, which is in turn superior to properties with hydroxypropyl acrylate. When used in combination with MF, environmental resistance is improved to approach that with IPDI isocyanurate and mar resistance is still excellent. TACT has also been evaluated with epoxy-functional acrylic resins. Coatings exhibit good mar and environmental etch resistance [503]. A combination of TACT and MEKO blocked HDI isocyanurate have been used as cross-linker for acrylic clear coats with good mar and environmental etch resistance [504]. In the same patent, use of TACT as a supplementary cross-linker in an epoxy-functional acrylic, acid-functional polyester, decanedioic acid clear coat improves mar resistance. Combinations of TACT and MF resins have been used with acrylic resins to give clear coats that combine good environmental etch and mar resistance [505].

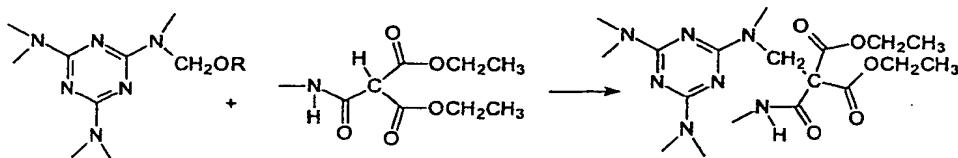


Fig. 13. Reaction of MF resin with the activated hydrogen of an amide–ester [498].

Also, base coats have been formulated using TACT with hydroxy-functional acrylic and polyester resins; excellent environmental etch and mar resistance is reported with clear coats made with epoxy-functional acrylic resin and a diioc acid [506]. High solids coatings with good cross-link density are formulated with a polyester diol and TMP triglycidyl ether with 4-dimethylaminopyridine catalyst [507]. TACT is used as a supplemental cross-linker in epoxy-functional acrylic, highly branched acidic polyester clear coats [508].

Blocked isocyanates have also been used as co-cross-linkers with trialkoxysilyl-functional acrylic resin clear coats; environmental etch resistance is enhanced [509]. Clear coats are formulated with poly(vinylidene fluoride) and acrylic resin with a blocked isocyanate [510]. MEKO blocked HDI or IPDI isocyanurates are used as cross-linkers for hydroxy-functional perfluoropolyether-based clear coats [511].

Use of blocked isocyanates in waterborne 1K clear coats has also been investigated. A water-reducible acrylic resin with an IPDI-based DEM blocked isocyanate and an MF resin are used in a clear coat [512]. A hydroxy-functional acrylic resin is prepared and then acrylic acid is polymerized in the solution after neutralizing with DMAE, the resin is dispersed in water and MEKO blocked HDI isocyanurate is added as a cross-linker [513]. A clear coat is formulated with MEKO blocked IPDI isocyanurate and a polyester/acrylic graft copolymer made by reacting a TMP-based polyester with the glycidyl ester of versatic acid followed by graft polymerization with a hydroxy- and carboxylic acid-functional acrylic resin, neutralized with DMAE and dispersed in water [514]. An MEKO blocked hydrophilically modified HDI isocyanurate is used to formulate a clear coat with a water-reducible acrylic/polyester graft resin [515]. Mixtures of high HMMM content MF resins and MEKO blocked IPDI can be used as cross-linkers for water-reducible trialkoxysilyl-functional acrylic resins [19]. An emulsion of a DMP blocked HDI isocyanurate modified, so that it readily emulsifies in a hydroxy-functional acrylic latex has been suggested as a binder for clear coats [53]. A waterborne coating is prepared by reacting the isocyanate groups on a TMI, glycidyl methacrylate, acrylic copolymer partially with diethanolamine and blocking the remaining isocyanates with MEKO [516]. A waterborne 1K clear coat is formulated with a graft copolymer from an MEKO blocked TMI hydroxy-functional acrylic resin grafted with another acrylic made from HEA and dimethylaminopropyl methacrylate neutralized with acetic acid [517]. A water-dispersible MEKO blocked IPDI isocyanate has been used to make clear coats with water-reducible acrylics or solvent-free waterborne clear coats with PUDs [7,518]. With water-reducible acrylic resins, TACT gives similar properties to those obtained with solvent-borne coatings [519]. Water-reducible polyester resin and MEKO blocked HDI isocyanurate are used to formulate a base coat [520]. Achieving adequate orientation of aluminum flake in spite of the low solids can be a problem. Rheology

modifying cross-linked microparticles to improve leveling of waterborne metallic base coats are prepared from aqueous dispersions of amine salts of hydroxy- and carboxylic acid-functional polyesters and DEM blocked IPDI/TMP prepolymer [521]. Blocked isocyanates and MF resins are used to cross-link water-reducible acrylic resins in clear coats that have an acrylic gel in the formulation to improve sag control [522].

Pigmented monocoats (single topcoats) have been formulated with a carboxylic acid- and hydroxy-functional acrylic resin, an epoxy and hydroxy-functional acrylic resin, and a mixture of blocked isocyanates [523]. Another monocoat is formulated with a hydroxy- and carboxylic acid-functional acrylic, an epoxy- and hydroxy-functional acrylic, a hydroxy-functional polyester, a blocked isocyanate, and MF resin [524]. Monocoats with improved environmental etch resistance have also been formulated with TACT as a supplementary cross-linker and with epoxy-functional and carboxylic acid-functional acrylic resins [504]. Waterborne blocked isocyanate coatings for trucks have been commercialized [525]. A waterborne automotive coating has been formulated using nonylphenol blocked TDI polyether polyol prepolymer, a PUD, and MF resin as a co-cross-linker [526].

Powder clear coats are of increasing interest to reduce VOC emissions. A 1,2,4-triazole blocked blend of HDI isocyanurate and HDI has been used as a cross-linker for acrylic resin powder clear coats [527]. A clear coat with good flow properties is formulated with CL blocked partially trimerized IPDI and a graft copolymer of a polytetrahydrofuran with a hydroxy-functional acrylic resin [528]. 1,2,4-Triazole blocked HDI isocyanurate is used with hydroxy-functional acrylic and polyester resins to formulate a clear coat [529]. A fluorocarbon-based powder clear coat is formulated with a blocked isocyanate and a chlorotrifluoroethylene copolymer [530]. Powder coatings for automobile wheels that provide good corrosion protection are formulated with blocked IPDI, epoxy resin, and acrylic resin [531]. Powder coatings that resist film imperfections such as cratering during application are formulated with combinations of hydroxy-functional polyester and acrylic resins with a blocked IPDI polyisocyanate [532].

Many of the powder coatings that have been patented are based on using epoxy-functional acrylic resins with two cross-linking reactions, first the epoxy groups react with difunctional carboxylic acids followed by reaction of isocyanate groups from a blocked isocyanate with the hydroxyl groups that are generated by the epoxy reaction. In some cases, the acrylic resin used is both epoxy- and hydroxy-functional. A combination of IPDI uretdione, hydroxy-terminated 1,4-butanediol caprolactone polyester, glycidyl methacrylate acrylic resin, and a dicarboxylic acid has been patented particularly for use as a powder clear coat for automobiles [533]. MEKO blocked H₁₂MDI and dodecanoic acid are used as co-cross-linkers for epoxy-functional acrylic resin powder clear coats [534]. Powder clear coats

using CL or MEKO blocked H₁₂MDI/TMP prepolymer [148], CL blocked partially trimerized IPDI [535], and an MEKO blocked mixture of HDI isocyanurate and a urethane modified H₁₂MDI polyisocyanate [536] with epoxy-functional acrylic resins have been patented. An automotive powder coating is formulated with CL blocked IPDI polyisocyanurate, a carboxylic acid-functional polyester, and an epoxy- and hydroxy-functional acrylic resin [537]. Pigmented powder coatings have been formulated with CL blocked partially trimerized IPDI, a graft copolymer made by reacting the carboxylic acid groups on a carboxylic acid- and hydroxy-functional polyester with the epoxy groups of an epoxy- and hydroxy-functional acrylic resin, and a crystalline diol to improve leveling [538]. The second color of two tone color automotive coatings is a pigmented powder coating made with blocked isocyanate, epoxy-functional acrylic resin, and dodecanoic acid applied over a base coated clear coated automobile with the desired areas free of masking that covers the balance of the car [539].

An aqueous powder dispersion of DMP blocked IPDI 2-ethyl-1,3-hexanediol prepolymer and an acrylic polyol clear coat is applied by conventional electrostatic spraying [540]. Aqueous dispersions of a blocked isocyanate acrylic powder topcoat are applied by conventional electrostatic spraying [13]. Rather than dispersing a powder coating in water, a fine particle size powder coating can be prepared in an aqueous medium. For example, a mixture of a water-reducible hydroxy-functional acrylic resin, a polyester, and DMP blocked IPDI isocyanurate is neutralized with DMAE, dispersed in water, and processed through a jet disperser to achieve a small relatively uniform particle size [541].

Primers for polypropylene are formulated with a hydroxy-functional acrylic resin with a partially blocked HDI isocyanurate and chlorinated polyolefin [542]. Coatings for polypropylene bumpers are formulated with polyester or acrylic polyols and blocked HDI isocyanurates [543] or a combination of blocked isocyanate and MF resin [544]. Pigmented coatings for polypropylene bumpers that cure at 120°C have been formulated with hydroxy-functional acrylics and polyesters with MEKO blocked HDI isocyanurate using dibutyl tin maleate as a catalyst [545]. The same catalyst was used with a hydroxy-functional acrylic resin and MEKO blocked HDI isocyanurate to formulate clear coatings. Clear topcoats for plastic bumpers are formulated with acrylic resins, blocked isocyanate, and MF resin [546]. Clear coats for use over plastics with improved scratch and chemical resistance are formulated using a hydroxy-functional polyester with a DMP blocked IPDI isocyanurate partial adduct of a 3-trialkoxysilylpropylamine that was reacted with diethyl maleate, and, in turn, the alkoxysilyl groups are reacted with hydroxyl groups on the surface of SiO₂ particles [547]. The coating is baked at 120°C for 1 h. Other coatings for plastics are discussed in Section 5.6.

5.4.2. Primers

A large number of patents disclose primers for application over steel that has been E-coated with cationic electrodeposition coating. In addition to providing a layer with good intercoat adhesion to the electrocoat primer and to the topcoats applied over it, many of these primers are formulated to serve as anti-chipping coatings. An MEKO blocked TDI-terminated polyether polyol is used with a polyester in formulating chip resistant coatings [548]. MEKO blocked-TDI-terminated polyol, an HDI-based hydroxy-terminated polyurethane, and a hydroxy-terminated polyester are used to make a chip resistant coating [549]. An MEKO blocked TDI/TMP polyether polyol, a hydroxy-terminated polyester, and pentaerythritol tetrakis(β-mercaptopropionate) are used as the binder in a low bake chip resistant primer [550]. A chip resistant primer is formulated with MEKO blocked MDI-terminated polyester and a hydroxy-terminated polyamide-polyether-polyester [551]. A series of patents discloses the use of hydroxy-terminated polyesters made from BPA epoxy resins with MEKO blocked isocyanates in high solids chip resistant primers [552]. An epoxy-terminated polypropylene glycol resin with a BPA epoxy resin with an acetone oxime blocked MDI prepolymer cross-linker gives high solids chip resistant coatings [553]. A low temperature curing, chip resistant primer with superior exterior durability is formulated with an ethyl acetoacetate blocked IPDI caprolactone polyol prepolymer (made using Zn(AcAc)₂ catalyst [554]. DEM blocked MDI that has been partially converted to allophanates with *n*-butyl alcohol is used in a chip resistant primer [555]. A blocked isocyanate/polyol chip resistant primer is formulated with a resin treated CaCO₃ [556]. A blocked isocyanate, a polyester, and an acrylic resin are formulated to give a chip resistant primer [557].

MEKO blocked TDI-terminated TMP/polyol, a polyester polyol, and an amine-terminated polyamide are used as a binder for chip resistant primers [558]. An MEKO blocked TDI prepolymer with TMP and polyethylene glycol is used with an amine-terminated polyamide and polyethylene glycol [559]. A CL blocked TDI-terminated TMP polyol prepolymer is used with the diketimine of DETA to make a low bake chip resistant primer [560]. MEKO blocked MDI-terminated polyether polyol, a hydroxy-terminated polyurethane, and oxypropylated ethylenediamine are used to make a chip resistant primer [561]. 2,4-Xylenol blocked MDI-terminated polyether polyol prepolymer is used to cross-link a DETA-propylene oxide adduct in a chip resistant primer [562]. Epoxy resins, polyester polyols, and blocked isocyanate are used to make chip resistant coatings [563]. A blocked isocyanate-terminated resin, an epoxy resin, and adipic acid dihydrazide are used to make chip resistant coatings [564]. A chip resistant primer is formulated with a CL blocked TDI-terminated TMP polyether polyol prepolymer and a polyoxypropylenetriamine [565].

A polyester, blocked isocyanate, epoxy-functional polybutadiene binder is used in making chip resistant primers

[566]. An alkyd coating cross-linked with a blocked isocyanate is said to have good adhesion to E-coat and resistance to chipping [567].

When greater resistance to yellowing is needed, aliphatic polyisocyanates are used. MEKO blocked HDI isocyanurate is used with a hydroxy-functional polyester to make a high solids chip resistant coating [568]. A blocked HDI-terminated polyester polyol and a hydroxy-functional acrylic resin are used to formulate a chip resistant coating [569]. An MEKO blocked HDI biuret isocyanurate-terminated polyol and a hydroxy-terminated polyurethane are used in a chip resistant coating [570]. Another chip resistant primer is formulated with ethyl acetoacetate blocked HDI biuret and a hydroxy-functional polyester [571]. Chip resistant primers are formulated with an MEKO blocked H₁₂MDI polypropylene diol and triol prepolymer [572] or a combination of MEKO blocked HDI and H₁₂MDI prepolymers with a combination of hydroxy-functional polyester and acrylic resins [573] and bis(4-amino-3-methylcyclohexyl)methane. An MEKO blocked H₁₂MDI/polyether diol and triol prepolymer with two or more blocked NCO groups per molecule is used with bis(4-amino-3-methylcyclohexyl)methane and *N,N*-bis(aminopropyl)dimethylaminohydantoin to formulate chip resistant primers for use over E-coats [574]. MEKO blocked H₁₂MDI/TMP polytetramethylene glycol prepolymer with a polypropyleneoxide triamine, catalyzed with methyltriethylammonium octanoate or *N*-8-nethyl-1,8-diazabicyclo[5.4.0]-7-undecene octanoate is used in formulating a non-yellowing chip resistant primer [575]. MEKO blocked H₁₂MDI-terminated polyether polyol [576] or MEKO blocked TDI prepolymer [577] are used with an amine-terminated polyamide in formulating a chip resistant primer. An MEKO blocked TMI-acrylic copolymer is used with a hydroxy-terminated polyester in a chip resistant coating [578]. A chip resistant primer is formulated using, e.g., an oligomer synthesized by a Michael addition of diethanolamine to 1,6-hexanediol diacrylate with acetophenone blocked IPDI [579].

High solids primers are formulated with blocked isocyanate-terminated oligomers made from butyl alcohol half-blocked IPDI reacted with 1,6-hexanediamine [580] or a diol from the reaction of an epoxy resin with an aliphatic diol [581], the diol from reacting a BPA epoxy resin with 2-ethyl-1,3-hexane diol, and an MF resin. Another primer is formulated with ethyl alcohol half-blocked IPDI reacted with 1,6-hexanediamine and BPA epoxy resin [582]. Half ethyl alcohol [583] *t*-butyl alcohol [584] blocked IPDI is reacted with ethanolamine to make an oligomer with terminal blocked isocyanate groups used as a cross-linked for BPA epoxy resin. A similar primer is made in which the ethyl alcohol half-blocked IPDI is reacted with 1,6-hexanediamine to make the oligomeric cross-linker.

An automotive undercoating has been formulated with an encapsulated TDI uretdione and a hydroxy-functional acrylic resin [585]. In one case the uretdione was encapsulated by dissolving in acetone and then precipitating in water with vigorous agitation and in another case by dissolving it in cyclohexane and adding a small amount of ethylenediamine with vigorous agitation.

A chip resistant waterborne primer is formulated with an anionic PUD having an MEKO blocked mixture of H₁₂MDI, HDI isocyanurate, and HDI uretdione, hydroxypivalic acid, neutralized with DMAE and diluted with water and mixed with another PUD that is hydroxy-functional [586]. The mixed polyisocyanates have an average of about 2.5 blocked NCO per molecule. An aqueous PUD of a polyester diol, DMPA, TMP, 1,6-hexanediol, MDI (or) IPDI blocked with MEKO and neutralized with DMAE is used with a hydroxy-terminated polyester in a primer for application over E-coated metal [587]. An MEKO blocked PUD polyurethane made from DMPA and TDI is reacted with hydroxy-terminated polyester-polyurethane made TDI, tripropylene glycol, isononanoic acid, isomerized linoleic acid, pentaerythritol, and isophthalic acid, the product is neutralized with DMAE, and cross-linked with an MEKO blocked combination of HDI isocyanurate and uretdione as the vehicle for a waterborne, chip resistant primer-surfacer [588]. A cationic waterborne primer-surfacer is formulated with HDI isocyanurate and a urethane/epoxy/amine polymer neutralized with acetic acid and diluted with water [589]. A waterborne chip-resistant primer is formulated with a hydroxy-functional acrylic-alkyd graft copolymer and an MEKO blocked TDI/TMP adduct [590] or with MEKO blocked HDI isocyanurate [591]. A waterborne chip-resistant primer is formulated with an ethoxyethyl alcohol blocked carboxylic acid-functional polyurethane prepared from DMPA and TDI which is reacted with a water-reducible polyester resin and then dispersed in water with DMAE and a combination of MEKO blocked HDI isocyanurate and MF resin [592]. A waterborne chip resistant primer is formulated with a carboxylic acid-functional styrene/butadiene latex with an MEKO blocked HDI/polyethylene glycol monomethyl ether cross-linker [593].

Vinyl plastisols containing blocked isocyanates have been widely used as the principal binder in chip resistant coatings. Several of the plastisols cited here are also said to be useful as sealants and others cited in Section 6.5 on sealants are also said to be useful as coatings. In some cases, plastisol coatings foam after application by reaction with water, incorporation of calcium oxide as one of the pigments minimizes this problem [594,595].

A blocked isocyanate is used with a polyester in formulating a plastisol chip resistant coating [596]. HDI isocyanurates blocked with a combination of *t*-butyl alcohol and MEKO [597] or 2EH and MEKO blocked HDI biuret [598] are used as a cross-linker in a plastisol that resists discoloration on baking with good adhesion. Nonylphenol blocked aromatic isocyanate [599], xylenol blocked isocyanate HDI biuret [600], and alkylphenol blocked isocyanate-containing [601] plastisols have been patented. 2-EH *p*-hydroxybenzoate blocked TDI [595] and

TDI isocyanurate [602] are reported to give less yellowing in a plastisol than nonylphenol blocked TDI. IEM acrylic resins blocked with a combination of isopropyl alcohol and 3,5-xylenol [603] or MEKO [604] have been used in PVC primers.

A plastisol coating containing PVC, hydroxy-functional PVC, amine-functional polyamide, and a blocked isocyanate give good chip resistance properties and intercoat adhesion [605]. A non-yellowing plastisol with a blocked isocyanate and amine-terminated polyamide has been patented [606]. MEKO blocked TDI [607] and a xylenol blocked isocyanate [608] with an amine-terminated polyamide have improved adhesion and chip resistance compared to coatings without the blocked isocyanate. A combination of blocked isocyanate and epoxy resin with dicyandiamide in a plastisol coating has been recommended for color stability [609]. A plastisol primer formulated with an MEKO blocked tetramethylxylene diisocyanate polytetramethylene glycol with bis(4-amino-3-methylcyclohexyl)methane is a stable compound in contrast with a similar primer using MDI [610].

A zinc-rich primer is formulated with a BPA epoxy resin, a blocked isocyanate, an imidazole catalyst, and a carboxylic acid- and hydroxy-functional ethylene/vinyl acetate copolymer [611]. A waterborne primer said to be especially useful for bonding window glass is formulated with an MEKO blocked PUD [612].

A plastisol chip resistant underbody coating is formulated with an MEKO blocked HDI prepolymer with a hexahydroxypolyol [613]. A plastisol with a blowing agent, a blocked isocyanate prepolymer, and amine-terminated polyamide is applied to the underbody and baked after the automobile bodies are coated [614]. A sound deadening underbody coat contains PVC resin, cross-linkable PVC, blowing agent, and a blocked isocyanate cross-linker [615] or a similar product using amine-terminated polyamide instead of the cross-linkable PVC [616].

Powder primer surfaces are being used over E-coat primers. For example, CL blocked IPDI has been used with a hydroxy-functional acrylic resin and a small amount of crystalline TMP; the TMP melts before significant cross-linking reducing viscosity of the melt and thereby improving leveling [617]. A powder primer for use over an E-coat is formulated with a blocked IPDI with a combination of hydroxy-functional polyester and acrylic resins [618]. There is the advantage that the powder primer does not cause cratering of adjacent areas that have been sprayed with an acrylic powder primer.

5.5. Insulating coatings for wire

The first blocked isocyanates to be used commercially in wire coatings were phenol blocked isocyanates; they are still used in many applications. Phenol itself and cresols, especially *m*-cresol are widely used. In most other applications, phenols are not used because they would be driven off into the atmosphere on curing. However, wire coating lines were

already set up using phenols as solvents. The equipment was already available to incinerate the phenol, recovering the beneficial fuel value of the phenol while simultaneously taking care of toxic emission possibilities [619]. Ref. [619] gives an excellent review of blocked isocyanates in wire coating up to the date of its publication.

A study of the relationship of molecular weight of polypropylene glycol, ratio of polypropylene glycol to TMP, and the effect of substituting polyethylene glycol for the polypropylene glycol using half phenol blocked TDI as a cross-linker on mechanical properties and wire enamel performance has been published [620]. Best results were obtained with low molecular weight polypropylene glycol and a ratio of diol to triol of 3–2 or lower.

Phenol blocked TDI diethylene glycol prepolymer is used as a cross-linker for polyester polyol in wire enamel coatings [621]. A series of mixed cresol blocked 4,4',4''-triphenylmethane triisocyanate and a TDI/trifunctional polyol prepolymer were studied for use with poly(ethylene terephthalate) resins in wire coatings, the TDI derivatives gave more flexible films [622]. Addition of a small amount of propionic acid permits control of the balance between gel time and cure speed with phenol blocked isocyanates and hydroxy-terminated polyesters [623].

The effect of using different levels of THEIC as one of the polyols in a polyester with blocked TDI on the properties of wire coating on thermal and insulating properties has been studied [624]. Rather than starting with THEIC, it can be synthesized *in situ* from ethylene glycol, ethylene carbonate, and hydrocyanuric acid and then transesterified with dimethyl terephthalate; the resultant polyester is used with phenol blocked TDI isocyanurate and a phenolic resin to make a wire enamel with superior properties and lower cost [625]. Phenolic blocked TDI/TMP prepolymer, phenoxy resin, phenolic resin, and MF resin have been used for wire coatings [626]. A polyol formed by reacting BPA epoxy resin with caprolactone cross-linked with a mixture of phenol blocked TDI and TDI trimer gave insulated wire with desirable properties [627]. Polyurethanes from the reaction product of BPA, polyols, with polymeric MDI using cresol blocked polymeric MDI as cross-linker coated on wire and baked at 380°C gave wires that are solderable at 360°C [628]. Use of combinations of CL and phenol blocked TDI/TMP with hydroxy-terminated polyesters has been patented [629]. A TDI/ethylene glycol prepolymer blocked with diethylene glycol monomethyl ether with a polyester resin is said to have a wider baking range than a coating with phenol blocked TDI/ethylene glycol prepolymer [630]. Mixed xylenol CL blocked MDI is used in wire enamels with hydroxy-terminated polyesters [631]. DEM blocked IPDI isocyanurate [632] and 2-phenylimidazoline blocked IPDI [633] have been patented for use as a hardener for wire enamels. An *m*-cresol blocked MDI/spiroacetal glycol with an epoxy resin gave improved performance compared to a coating without the spiroacetal glycol [634]. MDI partially converted to carbodiimide blocked with 3,5-dimethylphenol

is used with a polyester polyol to prepare wire coatings [635].

A polyester-urethane-urea wire coating based on cresol blocked TDI, melamine, and a hydroxy-terminated polyester with the aldimine from butyraldehyde and aniline as a catalyst has been patented [636].

Polyester-polyurethane wire coatings are made with various phenols as blocking agents, a hydroxy-terminated polyurethane made by reacting TDI or MDI with TMP in the presence of pyridines, then mixed with a hydroxy-terminated polyester with xylene and phenols as solvents [637]. A polyester derived from THEIC, ethylene glycol, and dimethyl terephthalate is used with a xylenol, cresol blocked isocyanate-terminated prepolymer from the reaction of MDI with THEIC and ethylene glycol to obtain a wire coating with good thermal shock resistance and soldering properties [638]. A phenol blocked mixture of MDI and TDI is used with a polyether polyol in formulating a wire enamel, addition of about 10% THEIC to the coating accelerates curing [639].

Various polyamides also serve as the principal resin for wire coatings. Hydroxy-functional nylons are made by titanate-catalyzed exchange with ethylene glycol; such a product is used with phenol blocked TDI isocyanurate to make a wire coating [640]. A similar coating in which a hydroxy-terminated polyester is also included in wire enamel has been patented [641]. Polyamide wire coatings are made using polyamides, phenolic resin, and phenol blocked TDI/TMP prepolymer [642]. Cresol blocked MDI is used as cross-linking agents for combinations of polyamides, phenolic resins, BPA epoxy resins, and/or BPA epoxy resin reacted with diethylamine [643].

Several variations on polyamide-imide (Fig. 14) wire coatings with various phenol blocked isocyanates have been patented [644]. CL blocked mixed MDI/TDI and a polyamide-imide wire coatings with [645] and without [646] 2-methylimidazole. A polyamide-imide modified polyurethane insulating enamel is made from the reaction product of isophthalic acid, MDI, *m*-cresol, ethylene glycol, and trimellitic anhydride together with a hydroxy-terminated polyurethane shows good impact resistance, flexibility, and

adhesion, with a softening temperature of 240°C [647]. A polyamide-imide is reacted with a cresol blocked MDI TDI prepolymer and treated with a catalyst to convert isocyanates to carbodiimides with phenol blocked TDI isocyanurate [648].

Heat-resistant fast-soldering coil magnet wire enameling is done with a mixed cresol/phenol blocked MDI/TMP prepolymer with a polyester-imide [649]. A heat-resistant urethane-amide-urea wire enamel is formulated with a cresol blocked MDI trimellitic anhydride reaction product, a hydroxy-terminated polyurethane, and the aldimine from butyraldehyde and aniline (catalyst) [650]. A varnish made from the reaction product of MDI with trimellitic anhydride and cresol blocked stearyl isocyanate give good properties and a softening point of 415°C [651]. A combination of amine-terminated polyamide, CL, 4,4'-diaminodicyclohexylmethane, adipic acid, and polyhydantoin with phenol blocked TDI/TMP prepolymer gave coated wire with a softening point of 193°C compared to 150°C for a polyamide coating [652]. Benzyl alcohol [653], CL blocked MDI [654], and pyrrolidone [655] have been patented for use as blocking agents in polyamide-imide wire coatings.

Carbodiimides with the free isocyanate groups blocked with phenols have been recommended for use in wire coatings; the reference provides an excellent overview of the synthesis, catalysis, and uses of carbodiimides in wire enamels [619]. Cresol blocked MDI partially converted to a carbodiimide and uretonimine polyisocyanate, TDI/TMP hexanediol prepolymer, or hydroxy-terminated polyurethane, and an aldimine from butyraldehyde and aniline (catalyst) are patented for wire enamel [656]. Cresol blocked MDI partially converted to a carbodiimide and uretonimine polyisocyanate reacted with trimellitic anhydride is used with tris *N,N',N''*-tris(2-hydroxyethyl)triazine in wire enamels [657]. A polyimide wire coating made by polymerizing 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 2,4-toluenediamine, and bis(4-diaminophenyl)methane in *m*-cresol followed by heating with cresol blocked MDI and coated on copper wire to give a coating with good insulating properties and a softening temperature of 510°C

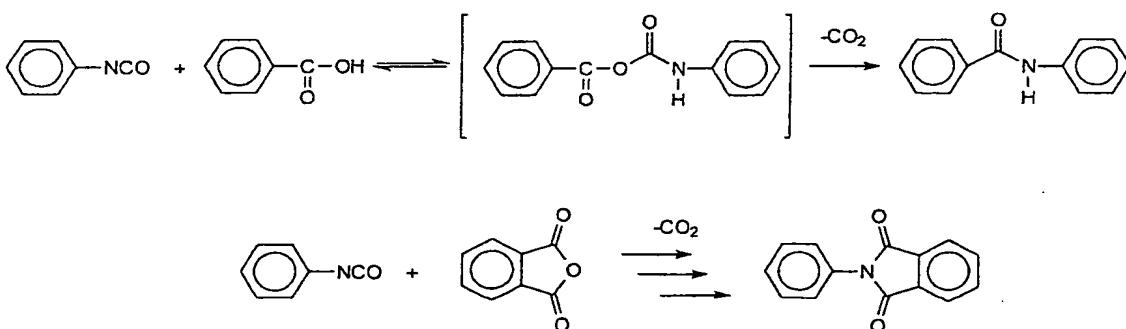


Fig. 14. Amide-imide formation.

[658]. A polyester-imide wire enamel is formulated with a cresol blocked MDI/TMP prepolymer [659]. A polyether-polyimide with phenol blocked TDI isocyanurate gives an enamel with a high cut-through temperature [660].

A cresol blocked mixture of TDI and MDI is partially converted to the carbodiimide derivative and used with the monomethyl ester of maleic acid to give hydantoin cross-links [661]. Polyhydantoin wire enamels have been made using partially CL blocked MDI, converting to a carbodiimide then reacted with monomethyl maleate to form a polyhydantoin substituted with acyl urea groups [662]. These substituted polyhydantoins can be further reacted with trimellitic anhydride to make a wire enamel [663].

Poly(vinyl formal), phenolic resin, alkyd resin, and phenol blocked TDI/TMP prepolymer is used as a wire coating [664]. Other patents also cover use of poly(vinyl formal), with various other components such as phenol blocked MDI, epoxy resin, and phenolic resin to make wire enamels [665]. Poly(vinyl butyral), cresol blocked MDI, and DMAE gives faster cure and higher heat resistance than the coating with DBTDL instead of DMAE [666]. Poly(vinyl butyral) with cresol blocked MDI has been patented for use as a wire coating [667]. Epoxy/phenolic resins with phenol blocked isocyanate have been patented as magnet wire enamels [668].

Self-bonding insulated coated wire coated with an acrylic polymer made from a monomer made by reacting HEA with half-phenol-blocked TDI, HEA, and methyl acrylate gave coils which showed higher tensile adhesion than poly(vinyl butyral) coated wire [669]. Heat-resistant self-bonding wire enamels are made with a polyether polyol, polysulfone, polyurethane, and phenol blocked TDI/TMP prepolymer [670]. Self-bonding wire coatings are made with a polyester triol, polyamide, and phenol blocked TDI/TMP prepolymer, catalyzed with tetrabutyl titanate [671].

A dimethylformamide solution of a polyamide-polyimide, phenoxy resin, blocked isocyanate coating was applied to wire, in line it was immersed in water and then cured; line speed was faster and a lower temperature required for cure than with the conventional solvent coating [672].

Waterborne coatings for wire are made using a CL blocked IPDI condensate with tartaric acid and a water-reducible polyester [673]. Anionic electrodeposition coatings of phenol blocked TDI/TMP prepolymer with a hydroxy-terminated polyester and a water-reducible acrylic resin for wire have been patented [674]. Phenol blocked TDI reacted with a polyester polyol was dispersed in water and methyl methacrylate, ethyl acrylate, triethylene glycol dimethacrylate, and acrylic acid were polymerized in the aqueous dispersion; after neutralization with ammonia, the coating was electrodeposited on copper wire. Waterborne polyether-imide wire enamels are cross-linked with phenol blocked TDI isocyanurate [675].

CL blocked TDI/hydroxyethyl acrylate-terminated resin with other acrylated resins and acrylate monomers is used to formulate solvent-free wire enamels curable to the B-stage by UV and then thermally cured have been patented [676]. A

UV cure and thermally cured coating is formulated with CL blocked TDI/HEA and other acrylate functional monomers for coating aluminum strips that are wound into coils [677].

A hot melt, storage stable polyester-polyurethane wire coating made from propylene carbonate, diethylene glycol, a hydroxy-terminated polyester, phenol blocked polymeric MDI, and zinc octanoate has a softening temperature of 240°C and good resistance to tinning [678]. A hot melt polyester-imide wire coating is formulated with *m*-cresol blocked TDI isocyanurate [679].

5.6. Coatings for plastics

Urethane coatings for plastics have the desirable features of high flexibility, abrasion and scratch resistance and many 2K urethane coatings are used on plastics. 1K coatings using blocked isocyanates would be highly desirable, but in many cases the plastic part being coated has a low heat distortion temperature, limiting the applications of blocked isocyanates. Blocked isocyanates with low deblocking temperatures can be used on some moderately lower heat distortion plastics. While higher temperature deblocking groups, such as CL, etc., are limited to materials with very high heat distortion temperatures such as polyphenylene sulfide or polyether ketones.

Abrasion- and scratch-resistant siloxane coatings including DEM blocked HDI biuret for polycarbonates exhibit good adhesion [680]. Another coating for polycarbonate is a three coat system: (1) a hydroxy-functional acrylic cross-linked with MF resin, (2) a thermoplastic acrylic resin with DEM/ethyl acetoacetate blocked HDI isocyanurate, and (3) a DEM blocked HDI biuret, a hydroxy-functional silicone resin, and a siloxane hydrolyzate [681]. DEM blocked HDI biuret, and a hydroxy-terminated polysiloxanes are also used for coating polycarbonate [682]. DEM blocked H₁₂MDI is recommended for acrylic clear coats over plastics [683]. Colloidal SiO₂ is treated with DMP blocked HDI reacted with diethyl *N*-(3-trimethoxysilylpropyl)aspartate and used in a hydroxy-terminated polyester coating to give an abrasion resistant coating on polycarbonate [684]. A polycarbonate sheet is primed with an acrylic primer then top coated with a UV absorber substituted hydroxy-functional acrylic resin, composite particles prepared from a trialkoxypropylsilane-modified acrylic resin that has been cross-linked with tetramethoxysilane, and MEKO blocked HDI isocyanurate to give a coated plastic with good exterior durability and surface hardness [685].

Primers for plastic lenses for glasses are made with acetylacetone blocked HDI isocyanurate and a polyether polyol [686] or MEKO blocked HDI isocyanurate with a polyester polyol [687]. Blocked isocyanate cross-linked coatings for plastic eye glasses have been patented that can be applied without blistering at thicknesses of ≥0.5 mm [688]. CL or 1,2,4-triazole blocked cycloaliphatic diisocyanate-terminated urethanes are formulated with a

polythiol, such as thioglycerol bis(2-mercaptopropionate) and a hydroxy-functional polyurethane.

MEKO blocked IPDI/TMP prepolymer is formulated with 2-aminoethyl methacrylate acrylic copolymers to make coatings for plastics that cure in 30 min at 110°C in comparison with 140°C when the same blocked isocyanate is used with a hydroxy-functional acrylic resin [689]. Aceto-acetic ester blocked HDI biuret and an MF resin are used with hydroxy-functional polyesters and polyether polyols to make high gloss coatings for urethane plastics [690]. Blocked isocyanates with hydroxy-functional polyesters and acrylic resins has been patented [691]. Use of benzyl-methacrylohydroxamate blocked MDI copolymerized with acrylic copolymers of DMAE methacrylate, HEA, methacrylamidopropyl(2-hydroxyethyl)dimethylammonium acetate, and other monomers for coating a variety of plastics has been patented [425].

A primer with good adhesion to vinyl resins is made from poly(methyl methacrylate), allylphenol-formaldehyde resin, and a CL blocked IPDI adduct [692]. An abrasion resistant coating for vinyl floor tile is formulated with a carboxylic acid-functional acrylic resin and blocked MDI [693].

A primer for nylon plastics is made with a CL blocked HDI-terminated reaction product of epoxy resin, azelaic acid, and diethanolamine, with MF resin [694]. A primer for polypropylene moldings is made with a blocked HDI isocyanurate, a hydroxy-functional acrylic resin, an epoxy resin, an MF resin, and 3-glycidyloxypropyltrimethoxysilane [695]. An aqueous dispersion of an epoxy resin CL blocked IPDI/prepolymer adduct powder coating for fiber-reinforced plastic moldings has been patented [696].

A waterborne anti-static coating for PET sheet is formulated with a water-reducible polyester, MEKO blocked MDI dispersed in an aqueous solution of poly(vinyl alcohol), and poly(2-aminoanisole-4-sulfonic acid) [697].

In-mold coatings for styrene/unsaturated polyester resins contain CL blocked oligomeric MDI, BPA epoxy methacrylate, styrene/unsaturated polyester and free radical initiator [698].

5.7. Other coatings

Glass bottles are often coated with a polyurethane coating to make them "shatter proof". Polyurethanes are particularly suitable because of their abrasion resistance and with the appropriate coreactant can be resistant to alkali washing; thus they are useful for returnable bottles. Recently a trend towards colored coatings has started. In contrast to typical green and brown bottles, color coatings are being made with organic pigments that will burn away when the glass is recycled. Coatings for glass that withstand sterilization are made using MEKO blocked IPDI and H₁₂MDI polyether polyol and dipropylene glycol prepolymer and triethanolamine [699]. Anti-shattering coatings for glass bottles are formulated using a water-dispersible cross-linker made by partially reacting H₁₂MDI with polyethylene gly-

col monomethyl ether, IPDA, and a dihydrazide from adipic acid and hydrazine and blocking the remaining NCO groups with MEKO, with a hydroxy-functional PUD as a coreactant [700]. In the use of MEKO blocked H₁₂MDI-terminated PUDs with hydroxy-functional PUDs made with H₁₂MDI coatings for glass, it was found, in general, that H₁₂MDI gave better performance than IPDI-based similar systems [51]. MEKO blocked hydrophilically modified polyisocyanates are used as cross-linkers for hydroxy-functional PUDs in glass coatings [701]. Another waterborne glass bottle coating is formulated with a water-dispersible blocked isocyanate made by reacting polypropylene glycol with a mixture of H₁₂MDI and IPDI then partially reacting the terminal NCO groups with dipropylene glycol and blocking the remaining ones with MEKO and a hydroxy-functional PUD [702]. The water dispersible acetate salt of the 2-dimethylaminomethylphenol blocked HDI isocyanurate has been suggested as a cross-linker for aqueous solutions of poly(vinyl alcohol) as a coating for glass [34]. A waterborne glass primer made from a TEA salt of an MEKO blocked HDI-terminated PUD from polybutadiene diol and DMPA provides good adhesion to glass for UV cure printing inks [703].

A few patents relate to uses of blocked isocyanates in can coatings, probably, primarily because of improved abrasion resistance with urethane coatings. For example, a blocked isocyanate is used with a hydroxy-functional vinylated alkyd in a white coating for cans [704]. A white exterior can coating can be made with a polyester and blocked isocyanate [705]. A waterborne can coating is made from a graft copolymer of acrylic ester, styrene, and acrylic acid onto a polyester/epoxy resin adduct, a benzoguanamine resin, and a blocked isocyanate [706]. Another waterborne can coating is made with a PUD from polytetramethylene glycol, DMPA, TDI, 2EH half-blocked TDI in NMP and a BPA epoxy resin which has been reacted with diethylethanolamine and thioglycolic acid, DMAE is added and the coating is reduced with water [707]. A waterborne coating for cans is formulated with an MEKO blocked isocyanate, water-reducible acrylic resin, and benzoguanamine resin [708]. TACT is used as a cross-linker for can coatings with a water-reducible acrylic resin and TMP triglycidyl ether [507]. A polyester-polyimide with cresol blocked TDI and phenol blocked TDI isocyanurate is formulated for an interior can coating [709]. A polyester film was coated with an adhesive comprising a hydroxy-functional polyester, epoxy resin, and IPDI uretdione 1,4-butanediol adduct to give a tack free film. The film could be laminated to tin free steel and heat treated for 1 min at 200°C for making sterilization proof coated cans [710].

MEKO blocked TDI/TMP prepolymer formulated with polypropyleneoxide diamines can be used in 2K coatings that cure at low temperatures. Secondary diamines, such as the *N,N*-diisopropyl derivative, give longer pot life than primary diamines [711]. An ambient temperature cure 2K coating is formulated with a 1,2,4-triazole blocked IPDI

polycaprolactone triol prepolymer and aliphatic polyamines and/or amine-terminated polyamides [712]. Similar 1K coatings can be formulated using diketimines [713]. A 2K ambient temperature cure coating is made with a 2,2,6,6-tetramethylpiperidine blocked IPDI polyethylene glycol prepolymer with DETA [714].

A 2K coating is formulated with MEKO blocked TMXDI and polyester polyols cure in 30 min at 125°C [715]. Ambient temperature cure light stable 2K coatings are made with 2,2,4,6-tetramethylpiperidine blocked IPDI with a polyester triol [716]. Use of HDI isocyanurate blocked with a 50/50 mixture of MEKO and 1,2,4-triazole cures a hydroxy-functional acrylic at 10°C lower temperature than with MEKO blocked HDI isocyanurate [170].

A chromium-free primer is formulated with a blocked isocyanate as cross-linker and a vanadium derived pigment [717] a similar primer is cross-linked with an MEKO blocked H₁₂MDI/polyester polyol prepolymer [718]. MEKO blocked IPDI polyisocyanate is used as a cross-linker for a corrosion resistant primer [719]. Low temperature curing (100°C for 30 min) coatings are formulated with *N,N'*-diphenylformamidine blocked trimerized HDI prepolymer with 1,3-butanediol [720]. Hydroxy-functional acrylic and polyester resins can be cross-linked with isopropyl alcohol blocked triisocyanatotriazine [386]. Derivatives of the reaction of carbamates with HMM resins are alcohol blocked isocyanates that can be used to cross-link hydroxy-functional acrylic or polyester resins (see Addendum, Section 3.2); the reaction is catalyzed by tetrabutyl diacetoxystannoxane [721]. 2,4,6-tris(butoxycarbamoyl)1,3,5-triazine is used as a co-cross-linker with HMM and hydroxy-functional acrylic resins [722]. Topcoats for military vehicles are made using a combination of MEKO blocked HDI isocyanurate and MF resin with a combination of hydroxy-functional polyester and acrylic resins [723]. Higher solid coatings can be formulated using methyl amyl ketone oxime blocked HDI isocyanurate as compared to MEKO blocked HDI isocyanurate because of the lower viscosity of the blocked isocyanates using methyl amyl ketone oxime [724]. MEKO blocked mixtures of TMXDI and HDI isocyanurate have been patented for use in making 1K coatings [725]. DMP blocked aliphatic polyisocyanates give coatings with good package stability and low cure temperatures [726]. DEM blocked H₆XDI-terminated prepolymers with 1,4-cyclohexanedimethanol are used as cross-linkers [727]. A polyester from undecylenic acid and a dialkyl maleate is reacted with an epoxy derivative is used with MEKO blocked

IDPI isocyanurate to make a coating vehicle [728]. Coatings with good abrasion and heat resistance are formulated with a colloidal silica with silanol groups on the surface that are reacted with an isocyanate-terminated prepolymer with MEKO blocked HDI isocyanurate as cross-linker [729].

Self-cross-linkable resins have been made by grafting an MEKO blocked TMI acrylic resin with HEA and other (meth)acrylate esters [730].

MEKO blocked isocyanates with oxadiazinetrione rings made by reacting HDI with CO₂ in the presence of tri-*n*-butylphosphine catalyst (Fig. 15) followed by reaction with triethylene glycol and blocking the remaining isocyanates with MEKO are useful in 1K coatings with acrylic polyols [731].

Some crystalline polyols are not soluble in aprotic solvents making them difficult to process. This problem has been overcome by partially reacting them with a blocked isocyanate, the resulting blocked isocyanate compound is used in a coating that is cured at higher temperatures. For example, a coating is prepared by blocking an H₁₂MDI polyester polyol prepolymer with MEKO, then partially reacting (about 1/3) with THEIC at 110°C, this blocked isocyanate coating has a very long storage life. The applied coating is cured at 150°C [732].

2-Acetoacetoxyethyl methacrylate blocked HDI is used with an acrylic polyol, dibutyltin diacetate, and peroxides to give a 1K coating that cures at 120°C [733]. DEM [734] and mixed DEM/ethyl acetoacetate [735] blocked IEM is used to make copolymers for 1K coatings. MEKO blocked TMI copolymer self-cross-linkable graft copolymers give stable coatings that can be cured at 100–120°C [69]. 2-Phenylimidazoline blocked IPDI diethylene glycol prepolymer with a hydroxy-functional polyester is used in formulating 1K coatings [736]. A CL or acetone oxime blocked mixture of IPDI and IPDI uretdione extended with a diol with a hydroxy-functional polyester gives a coating with reduced curing time, improved stability and reduced blocking agent emissions [737]. A 1K coating is made with a uretdione made by reacting an isocyanurate and butyl isocyanate in the presence of tris(dimethylamino)phosphine, stopping the reaction with H₃PO₄, and distilling off unreacted butyl isocyanate and its dimer and using the remaining dimer with an acrylic polyol [738]. MEKO blocked HDI polyisocyanate and a polyester polyol are formulated with a siloxane gel in an enamel [739]. Hydroxy-functional acrylic resins are used with MEKO blocked HDI polyisocyanate in making soil and chemical resistant coatings [740]. 1,2,4-Triazole

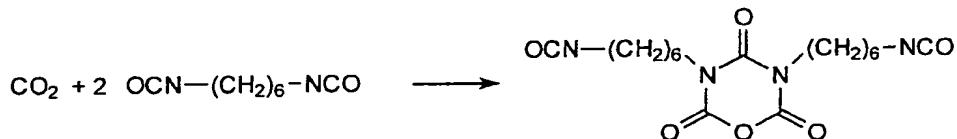


Fig. 15. Oxadiazinetrione formation.

blocked H₁₂MDI that has been reacted with a small fraction of an alcohol to convert part of the isocyanate groups to urethanes and a small amount of perfluoropolypropylene glycol monoether with a hydroxy-functional coreactant gives relatively high solid 1K coatings with lower surface free energies [741]. An abrasion resistant coating is formulated with an MEKO blocked TDI polyether triol, a polyether diol, ethylene glycol dimethacrylate, TEPA, and a peroxide initiator [742]. HDI/TMP prepolymer is trimerized to give an isocyanurate with an average functionality of 5, then blocked with a combination of DEM and ethyl acetoacetate using sodium methoxide as catalyst and neutralizing the catalyst with H₃PO₄ to improve stability is used to cross-link a hydroxy-functional acrylic resin [743].

Stable 1K coatings that cure in 20 min at 150°C can be formulated with a blocked isocyanate, such as nonylphenol blocked TDI/polyether diol and triol prepolymer, a ketimine, such as the diketimine from IPDA and MEK, and a compound that releases water with heat, such as a salt made by reacting phthalic anhydride with DETA [744].

Adhesion of anti-corrosion urethane primers to sand blasted steel is improved by partially blocking the isocyanate groups with a phenol such as 2-naphthol [745]. A primer for galvanized steel is formulated with an amine-modified BPA epoxy resin, polyfunctional amine, and MEKO blocked HDI isocyanurate [746]. A topcoat for primed galvanized steel is formulated with a hydroxy-functional polyester cross-linked with MEKO blocked H₆XDI prepolymer with dipropylene glycol and ethylene glycol [747].

Alkylphenol blocked TDI prepolymers have been widely used for flexibilizing BPA epoxy-amine coatings. They are particularly useful in protection and renovation of concrete structures. Refs. [748,749] review the effect of variables on the kinetics of the reactions and mechanical properties of films. Choice of the diamine can be particularly critical in designing the coatings; a blend of *m*-xylylene diamine and 3(4),8(9)-bis(aminomethyl)tricyclo[5.2.1.0]decane with nonylphenol blocked TDI and BPA epoxy gives a desirable combination of properties [748]. Intercoat adhesion to and flexibility of epoxy/amine primers is improved by adding an isononylphenol blocked TDI/prepolymer; differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) have been used to study the curing of such systems [749]. The isocyanate and the epoxy react with the amine groups; initial reaction of amines is faster with the blocked isocyanate than without it. The improvement in film properties is attributed to microphase separation.

High solids coatings made with non-aqueous graft copolymers of hydroxy-functional acrylic and polyester resins are used with a blocked isocyanate [750].

A waterborne coating is formulated with aqueous dispersions of BPA epoxy resins and a nonylphenol blocked TDI anionic PUD or nonylphenol blocked TDI water-dispersible prepolymer and bis(4-amino-3-methylcyclohexyl)methane [751]. A water-dispersible, uretdione-functional cross-linker is formulated with a mixed HDI uretdione and isocya-

nurate, DMPA, and a tertiary amine that is dispersed in water leading to urea links and used in a 2K coating with a water-reducible acrylic resin [752]. Single package coatings based on MEKO blocked polyisocyanate and a water-reducible acrylic resin gives equivalent properties to those obtained with 2K solvent-borne coatings [753]. MEKO blocked HDI isocyanurate is used to cross-link coatings formulated with water-reducible acrylic resins [11]. Waterborne coatings are formulated with dry powders of hydroxy-functional acrylic resins and CL blocked IPDI dispersed in water, surfactant, and polyethylene glycol [754].

TDI prepolymers with polyether polyols (molecular weight about 3000) are blocked with coumarin-indene or terpene hydrocarbon resins that are phenolic hydroxyl-functional for use in formulating flexible epoxy-amine coatings [755]. Since the blocking group is covalently bonded to the resin, no volatile blocking agent is emitted.

A 1K self-cross-linking, water repellent coating is prepared by copolymerizing, MEKO blocked IEM, acrylic ester, HEMA, and a vinyl-terminated polysiloxane [756]. Water repellent coatings for aluminum fin-structures are formulated with MEKO blocked H₁₂MDI fluorinated vinyl copolymers, and hydroxy-functional polysiloxanes [757].

A number of other waterborne coating systems have been patented. Aqueous non-ionic dispersions of BPA epoxy resins and a waterborne MEKO blocked HDI isocyanurate reacted with DMPA and neutralized with TEA give good quality films when baked at 140°C for 20 min [758]. An MEKO blocked HDI isocyanurate adduct with DMPA neutralized with TEA is used with an aqueous dispersion of BPA epoxy resin and a urethane resin to make a coating with good impact resistance [759]. A PUD with MEKO blocked MDI/polypropylene glycol, cyclohexyldimethanol, DMPA polyurethane is neutralized with TEA, diluted with water then chain extended with IPDA to make a waterborne coating [760]. An MEKO blocked PUD from polyethylene glycol, TMP, and TDI chain extended with ethylenediamine is used with non-functional acrylic latex to give a baked coating with superior abrasion resistance [761]. MEKO blocked HDI biuret and an HMMM resin are used as co-cross-linkers in a coating with a polyester and a PUD [762]. Partially MEKO blocked HDI was reacted with a high NH-MF resin and the product was used with a water-reducible polyester to make a waterborne coating with good flexibility and impact resistance [763]. A phenol blocked IPDI polyester-based PUD is used in an anti-corrosive paint [764]. A blocked isocyanate is used with a water-reducible polyester [765] or water-reducible acrylic resins [766] in waterborne coatings. Waterborne coating systems are made with water-reducible acrylic resins polymerized in a solution of ethyl alcohol blocked IPDI [15]. Another waterborne acrylic finish is cross-linked with water-dispersible CL blocked isocyanate prepared by reacting HDI with 2-*n*-butyl-2-ethyl-1,3-propanediol trimerizing and then reacting with a monomethyl ether of polyethylene glycol [40]. An aqueous dispersion of a NaHSO₃ blocked IEM copolymer

acrylic resin with hydroxyl-functionality is stable for 3 months and gives coatings with good water resistance [767]. MEKO blocked hydrophilically modified HDI polyisocyanurate permit formulation of waterborne coatings with lower VOC and give coatings with better appearance than conventional polyisocyanates [768]. Coatings formulated with low molecular weight oligopolyesters, the 2,2-dimethyloctanoic acid ester of the 2,3-dihydroxypropyl ester of 4-hydroxybenzoic acid, and acetone blocked HDI trimer with very low levels of VOC can be diluted to application viscosity with water [769].

A two package base coat for corrosion resistant linings for concrete surfaces consists of (1) a BPA epoxy resin, a nonylphenol blocked TDI prepolymer adduct, and a urethane acrylate polymer and (2) a modified cycloaliphatic amine and a modified polyamine [770]. 2K ambient temperature cure solvent free coatings for concrete are formulated with 2,2,4,6-tetramethylpiperidine blocked IPDI with polypropylene glycol and a diamine such as bis(4-amino-3-methylcyclohexyl)methane. A similar 1K coating is formulated with the same blocked isocyanate using the diketimine from methylisobutyl ketone and isophorone diamine [771]. An imidazole blocked TDI-terminated TMP/polyether polyol and a polyether diol prepolymer in water were applied as a primer for concrete [772].

Phenol blocked TDI/TMP prepolymers with phenoxy resins have been patented for use in coatings for rebars for reinforcing concrete structures [773].

A concrete bridge deck is reinforced and protected from water by seal coating. First the concrete bridge deck is coated with a two component waterborne epoxy coating, then before that coating is dry a polyester non-woven fabric is laid on the sticky surface followed by a coating consisting of a *t*-butylphenol blocked TDI polyetherpolyol prepolymer, a liquid BPA epoxy resin, coal tar pitch, and a diamine such as 1-(2-aminoethyl)piperazine [774].

Traffic paint based on hydrocarbon resin with added CL blocked cycloaliphatic isocyanate has been patented [775].

Stable 1K ambient temperature cure coatings can be made using a nonylphenol blocked TDI polyether triol diol prepolymer with an insoluble acetic acid salt of an amine such as hexamethylenediamine [776] or an internal salt such as the half phthalic amide of triethylenediamine [777] dispersed in it, epoxy resins can also be added to the coatings. Similar baking 2K coatings with several hour pot lives can be formulated with the same nonylphenol blocked TDI prepolymer with bis(4-amino-3-methylcyclohexyl)methane dispersed in it [778].

A gallic acid modified polyester cross-linked with a blocked isocyanate is used in a primer for steel with good adhesion and impact resistance [779]. The vehicle for an abrasion resistant 2K interior pipe coating is a BPA epoxy resin with isononylphenol blocked TDI polyether polyol prepolymer in one package and polyglycoldiamine in the other [780].

A coating for stainless steel is formulated with a hydroxy-functional fluorinated chlorotrifluoroethylene copolymer with vinyl ethers, an acrylic resin with a covalently bonded UV absorber, and MEKO blocked HDI [781]. Coatings for stainless steel are formulated with a blocked isocyanate, the DMAE salt of an epoxy phosphate resin and a hydroxy-functional acrylic resin [782]. A coating for galvanized steel is formulated with a blocked isocyanate and a water-reducible polyester [783]. Heat resistant coatings are made with phenol blocked TDI isocyanurate and a polyimide from 2,2-bis[4-(3,3)dicarboxyphenoxy]propane dianhydride with *m*-phenylenediamine copolymer [784]. Another heat resistant coating is made with MEKO blocked HDI isocyanurate with a polyamide-polyimide polymer [785].

UV or E-beam cure coatings that are also heat curable are made using a blocked isocyanate with an acrylate-functional resin [786]. MEKO blocked XDI/HEA adduct, epoxy resin methacrylate and additives are used in making a UV cure coating that also heat cures [787]. Another UV and thermal curing coating is formulated with MEKO blocked XDI and a BPA epoxy resin that has been reacted with acrylic acid and DMAE methacrylate [788]. A phenol blocked TDI adduct of a 2-hydroxy-(3-alkylphenoxy)propyl acrylate can be UV cured then heat cured [789]. UV coatings with accelerated cure as compared to other such coatings are made using isopropyl alcohol blocked isocyanatoethyl acrylate as a comonomer [790]; this was run at a temperature where one would not expect deblocking to take place. A base coat formulated with a polyester, blocked isocyanate, and polyethylene glycol acrylate is heat cured then over-coated with an electron beam curable acrylate-functional topcoat [791].

Wrinkle finishes are made using a blocked isocyanate polyester topcoat [792]. Another wrinkle finish uses a waterborne acrylic resin, aluminum pigmented base coat with a blocked isocyanate, followed by an acrylic/MF solvent-borne clear topcoat [793].

Chalkboard coatings are prepared using a thermosetting acrylic resin and a blocked isocyanate as the binder [794].

6. Adhesives and sealants

In addition to adhesives discussed in this section, adhesives used in mounting synthetic leathers to fabrics are discussed in Section 7.3, adhesives for use in laminating films to make coated fabrics in Section 8.3, adhesives for rubber applications in Section 9, and adhesives for electrical and electronic applications in Section 10.1.

6.1. Two package adhesives

In 2K epoxy-amine adhesives, addition of nonylphenol blocked TDI polypropyleneoxide polyol prepolymer to the epoxy package of an adhesive whose second package is a combination of *N*-cyclohexylpropylenediamine

and a mercaptan-terminated polypropyleneoxide polyol accelerates cure while retaining adequate pot life [795]. Phenol blocked MDI or HDI serve as latent catalysts for amine cured epoxy adhesives [796]. Oxime blocked MDI added to the epoxy package of a 2K epoxy–amine adhesive accelerates the heat cure while maintaining adequate pot life [797]. A 2,2,6,6-tetramethyl-4-oxopiperidine blocked IPDI polypropyleneoxide polyol prepolymer was mixed with a liquid BPA epoxy resin, IPDA, and 2,4,6-[tris(dimethylamino)phenol] (catalyst) to make an adhesive that cured in 1 week at room temperature or rapidly at 80°C [798]. Ambient temperature cure epoxy–amine adhesives using a 1,2,4-triazole blocked aliphatic isocyanate/polyglycol prepolymers show increased flexibility [799]. An epoxy adhesive with isopropylcyclohexylamine blocked TDI polypropylene glycol prepolymer and adipoyl dihydrazide and a tertiary amine catalyst was stable at 30°C for over 2 weeks and cured at 120°C in 1 h [800]. A primary amine with nonylphenol blocked IPDI for use in epoxy adhesive is made by reacting the half-blocked diisocyanate with the ketimine from MIBK and 2-aminoethyl alcohol then allowing the remaining ketimine groups to hydrolyze [801].

A wide range of monoisocyanates and diisocyanates blocked with imidazole have been evaluated as latent catalysts in epoxy adhesives, e.g., imidazole TMXDI gives an adhesive with good pot life and rapid cure at low temperatures [802].

An epoxy resin modified silicone adhesive for tiles is made from silicones, a BPA epoxy resin, and a blocked isocyanate [803]. An ambient temperature curing waterborne lining adhesive is formulated with MEKO blocked IPDI adduct with a monomethyl ether of polyethylene glycol and an aqueous dispersion of an ethyl acrylate/diacetone acrylamide copolymer [804].

2K adhesives for joining plastic automobile bodies consist of one component being a CL blocked TDI/polypropylene glycol prepolymer and the other being methyl methacrylate, ethylene glycol, *N,N,N',N'*-tetrakis(β-hydroxyethyl)ethylene diamine with benzoyl peroxide initiator. Sheets are coated, pressed together for 15 min at 80°C, and cured for 20 min at 140°C to obtain a high bond strength [805].

6.2. One package adhesives

1K adhesives have also been reported. MEKO blocked MDI/polypropylene glycol polyols prepolymer with a tri-functional amine-terminated polyol gives a solvent-borne adhesive that cures in 3 min at 160°C compared to 250°C for a conventional adhesive [806]. MEKO blocked HDI isocyanurate with *N*-di(2-hydroxyethyl)aniline gives an adhesive with a package stability greater than a month and curing in 2 h at 180°C [807]. A DMP and imidazole blocked MDI polypropylene prepolymer with a BPA epoxy resin and tris(imidazol-1-yl)triazine is used in formulating 1K adhesives with a low cure temperature [808]. DMP blocked HDI isocyanurate is used with a polyoxyalkylene triamine

in 1K flexible adhesives that cure at 120°C with a package stability of over 2 months since the blocked isocyanate is insoluble in the triamine [809]. The package stability can be extended further by addition of glycerol, which reduces solubility and increases polarity of the medium, which further reduces reactivity of blocked isocyanates. The glycerol does not react during cure but acts as a plasticizer. Adhesives with isononylphenol blocked TDI, a BPA epoxy resin, bis(4-amino-3-methylcyclohexyl)methane, and chlorinated polyethylene give superior adhesion in laminating vinyl films to plywood [810]. An adhesive for laminating polypropylene film to galvanized steel is formulated from the reaction product of a BPA epoxy resin with azelaic acid and diethanolamine with CL blocked IPDI, MF resin, and a maleated polypropylene [811]. Polypropylene film can be laminated with galvanized steel using an adhesive comprising MEKO blocked MDI, carboxylic acid-functional resins derived from epoxy resins and maleated polypropylene [812]. Use of pyrazoles, such as DMP, in adhesives has been recommended because of their low deblocking temperature and lack of toxic hazard. Furthermore, the pyrazole freed by the deblocking reaction promotes adhesion between several plastic and metal substrates as demonstrated by comparisons with phenol blocked isocyanates [813]. 3(5)-Methylpyrazole blocked isocyanates have been recommended for adhesives [814]. An ethylene/tetrafluoroethylene copolymer film with a colored polyester/MF/blocked isocyanate coating with a polyurethane polyol/blocked isocyanate adhesive is laminated to steel plate [815]. An adhesive for laminating polypropylene film to a printed polypropylene film is formulated with MEKO blocked HDI biuret and chlorinated polypropylene that has been reacted with maleic anhydride [816]. Adhesives for laminating polyester film are made with a plastisol containing 2EH 4-hydroxybenzoate blocked TDI isocyanurate [817]. A blocked isocyanate hydroxy-functional acrylic adhesive is coated on a printed acrylic sheet then put in a injection mold which is then filled with polypropylene [818]. An HDI uretdione with a polyester diol is used as a 1K adhesive for laminating PET film to steel [819]. Flexible structural adhesives are formulated with HDI prepolymer with polypropylene glycol and TMP with bis(3-allylphenol). Adhesives are formulated with a combination of a carboxylite acid functional acrylonitrile/butadiene rubber reacted with BPA epoxy resin and a p-aminophenol blocked IPDI polyether polyol prepolymer [820].

Bis(carboxymethyl)-bis(2-acryloyloxyethoxymethylamine, a methyl alcohol blocked isocyanate (see Addendum, Section 3.2), is used with a hydroxy-functional polyurethane prepared from TMXDI, HEA, and polycaprolactone diol and an azo initiator to formulate baking adhesives that cross-link with a combination of urethane formation and free radical polymerization [821].

A uretdione-functional adhesive with excellent vertical sag resistance is formulated using a uretdione-functional thixotropic agent prepared by the reaction of TDI uretdione

with a maleic acid polyester diol, and polyether diol and triol used with a uretdione-functional, amine-functional polyurethane made with TDI uretdione, a polyether triol and a polyether triamine [822].

Acetone oxime blocked TDI/TMP/polyethylene glycol forms a stable water dispersion when ammonium hydroxide is added to a pH of 8–9; it is used as an adhesive for laminating PET films [823]. Adhesives for labels have been formulated with a dibutylamine blocked IPDI, polyester diol, 1,4-butylene glycol, and hydrazine hydrate prepolymer with a hydroxy-functional acrylic resin [824]. Waterborne adhesives for laminating PET and PE films or polypropylene films to cardboard are made with an acrylic latex with MEKO blocked IPDI reacted with HEA and diacetone acrylamide as comonomers [79]. Waterborne adhesives for laminating rubber sheets, PET films, and vinyl film to plywood using a blocked isocyanate solubilized by using salts of taurine or glycine in making the prepolymer [37]. For example, an MEKO blocked HDI biuret prepolymer with hydroxy-terminated polybutadiene and sodium glycinate is used in a adhesive with ethylenediamine as a cross-linker.

Waterborne adhesives with blocked isocyanates have also been made. An adhesive for metal plates is formulated with a hydroxy-functional PUD and a water-dispersible 2EH blocked polyisocyanate prepared by reacting HDI with 2-n-butyl-2-ethyl-1,3-propanediol trimerizing and then reacting with the product of reacting polycaprolactone triol with maleic anhydride [40]. An isocetyl alcohol blocked water-dispersible isocyanate was emulsified and added to a butyl acrylate/vinyl acetate latex to give an aqueous adhesive with good lap shear strength [825]. MEKO blocked HDI isocyanurate dispersed in an aqueous solution of partially saponified polyvinyl acetate and a polyvinyl alcohol/SBR latex adhesive showed no change in viscosity after 1 month storage and bonded lauan veneers with good adhesion [826]. A plywood adhesive consists of a resole phenolic resin, acetylacetone blocked HDI polyisocyanurate, and starch [827]. A waterborne adhesive has been patented that uses *O,O'*-[*N,N'*-bis(hexamethylenecarbamoyl)hydroxy]ammonium chlorides as cross-linkers for acetoacetoxy-functional acrylic latex (the pH is adjusted to 6 with aqueous ammonia) [828]. The biscarbamoyl salt is made by acid hydrolysis of acetone oxime blocked HDI (Fig. 16). After application, the carbamoyl salts are thermally decomposed to afford primary amines that cross-link the polymer through formation of enamines with acetoacetate groups.

1K adhesives have been formulated using encapsulated particles of MDI surface treated with diamine, with TDI uretdione, ethoxylated 2,2-bis(4-hydroxyphenyl)propane

polyether diamine, polyurethane–urea with TDI and MDI, and ethylene/vinyl acetate/vinyl alcohol [829].

1K epoxy–amine adhesives formulated with a blocked isocyanate, methyldimethoxysilyl ethyl ether, and a ketimine, show good stability and adhesion to glass, aluminum, and mortar [830].

1-Cyanoethyl-2-phenylimidazole blocked MDI prepolymer with hexamethylenediamine has been used as a blocked catalyst in formulating epoxy adhesives [831].

Heat-activated adhesives are applied to, e.g., steel; the coated steel can then be laminated with heat to a plastic film. A polyester/cresol blocked MDI adhesive is coated on steel and dried; then heated to 195°C and laminated with a PVC film [832]. Another heat-activated adhesive uses a combination of MEKO blocked TDI-terminated polyether diol elastomer, bis(4-aminophenyl)methane, *N,N'*-bis(furfuryl)-1,6-hexanediamine, furfurylamine and *N,N'*-*m*-phenylenedimaleimide [833]. The coating is applied to a substrate that is then heated to 150°C for 4 min and immediately laminated to another piece of the substrate. Cross-linking occurs by a combination of isocyanate–amine reactions and diene/dienophile reactions. Composite vibration dampers are made by laminating metal sheets with MIBK oxime blocked TDI/castor oil prepolymer with a polyester and a BA epoxy resin adhesive [834].

A powder adhesive for bonding steel plates is made from IPDI isocyanurate that has been partially reacted with 1-octadecanol, a cyclic amide, and acetophenone oxime with a BPA epoxy resin [835]. A powder adhesive with the advantage that there is no volatile blocking agent is made with an IPDI uretdione extended with a hydroxy-functional polyester with an epoxy resin and 2-phenylimidazoline blocked IPDI that releases the imidazoline as a catalyst for epoxy reactions when the adhesive is heated [836]. Another uretdione powder adhesive is prepared with IPDI uretdione, a polyol, and an epoxy resin [837].

Adhesives for bonding coated polarized films have been patented [838].

6.3. Hot melt adhesives

The stability of blocked isocyanates permits formulation of thermosetting hot melt adhesives. CL blocked oligomeric MDI with a polyester diol gave an adhesive with a melting point of 117°C that is hot melt coated on a polyurethane foam and laminated with a decorated polyester film then cured at elevated temperature [839]. An ethyl 4-hydroxybenzoate blocked MDI polyester diol prepolymer with a low molecular weight diol or triol is used to

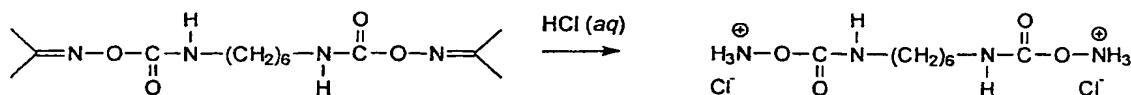


Fig. 16. Hydrolysis of an oxime blocked isocyanate to a carbamate salt.

formulate a hot melt adhesive for fiber glass reinforced plastics [840]. CL blocked IPDI is used in a hot melt adhesive with hydroxy-terminated polybutadiene [841]. Uretdiones provide a route to cross-linking without emission of blocking agent, thus a hot melt adhesive can be prepared using an ethylene/vinyl alcohol copolymer with IPDI uretdione in which the free NCO groups have been reacted with 1,4-butanediol and an alcohol [842]. Another approach to avoiding emission of blocking agent is the use of a phenolic resin in an adhesive as the blocking agent. Thus MDI blocked with a phenolic terpene resin with a copolymer of ethylene, HEA, and vinyl acetate, and another phenolic terpene resin gives a hot melt adhesive that can be cured at 180°C in 5 min [843].

A reactive hot melt adhesive prepared from a CL blocked MDI polyester polyol prepolymer extended with 1,4-butanediol is laminated with a surface layer of fabric [844]. A powder hot melt adhesive prepared from an *n*-butyl alcohol blocked isocyanate-terminated polyurethane from H₁₂MDI, a polyester diol, and ethylene glycol with a distearyl amine/stearyl isocyanate urea is applied to a polyester/cotton fabric, partially cured then heat laminated to a cotton knit fabric. The laminated fabric shows excellent wash and laundry resistance [845].

6.4. Film, transfer, and pressure sensitive adhesives

Film adhesives with blocked isocyanates have been prepared. A mix of partially saponified ethylene/vinyl acetate copolymer with 0.5% of cresol blocked MDI was kneaded and pressed to give an adhesive film that was used to bond aluminum sheet onto aluminum honeycomb [846]. Heat activated adhesive films are prepared from an encapsulated polyisocyanate, prepared by treating an aqueous dispersion on solid isocyanate particles with a polyamine, and a water reducible coreactant having a T_g above ambient temperature [847]. Similar adhesive films are formulated using encapsulated polyisocyanates prepared in a solvent media [848].

Flame retardant adhesive films for bonding sheets of polyvinyl fluoride film together for use in aircraft have been prepared with a mix of phenoxy resin, hydroxy-terminated urethane elastomer, MEKO blocked HDI isocyanurate, decabromophenylene oxide, and antimony and aluminum oxides [849].

An interlayer film for laminating glass sheets has been prepared from a partially hydrolyzed ethylene/vinyl acetate copolymer, ethylene/methyl methacrylate/maleic anhydride copolymer, and CL blocked IPDI ethylene glycol prepolymer [850]. A cationic PUD made with IPDI, polyester polyol, polyether polyol, and DMAE was blocked with DEM and dispersed in water acidified with HCl, coated, and detached from the support; the sheets were used to laminate glass [87].

Transfer adhesives have been patented. A polyester film with a release coating was printed with an acrylic ink and coated with an acrylic polymer adhesive containing

5% blocked isocyanate. The adhesive side of the film was pressed on glass at 200°C and the release coated polyester film was removed. The transferred sheet was coated with a polyurethane coating and cured 12 min at 160°C [851].

Pressure sensitive films and tapes have been made using blocked isocyanates. A hot melt, pressure sensitive adhesive contains a butyl acrylate/acrylic acid copolymer, with 3% of cresol blocked MDI, and 0.5% 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) catalyst was coated on a polyester film. The adhesive coated film was heated at 160°C for 10 min and cured at 70°C for 24 h. When the film was pressed on stainless steel plate it gave good peel strength and creep resistance [852]. Pressure sensitive tapes are prepared by coating a polyester film with phenol blocked TDI/TMP, a hydroxy-functional acrylic resin, and DBU catalyst [853]. A primed polyester film was coated with an adhesive from hydroxy-terminated polybutadiene and an MEKO blocked isocyanate and dried at 140°C for 5 min to give a pressure sensitive sheet with good adhesion and creep resistance on stainless steel [854]. A butyl acrylate/acrylonitrile/acrylic acid copolymer, dioctyl phthalate, *m*-cresol blocked HDI adhesive was melt extruded on a polyethylene film and cross-linked by an electron beam to prepare a tape for temporary protection of stainless steel [855]. A pressure sensitive masking tape for automobiles that releases with heat is prepared by coating a polyester film with a compound of acetoacetic ester blocked HDI biuret and a butyl acrylate/ethylhexyl acrylate/4-hydroxybutyl acrylate/acrylic ester copolymer [856].

A waterborne primer for sealing paper that is to be coated for release paper for pressure sensitive tape is made using an alcohol blocked isocyanate that has also been reacted with a polyoxyethylene-polyoxypropylene monoether as a cross-linker for poly(vinyl alcohol) [857]. Water-based, pressure sensitive adhesives for high temperature resistant masking tape is prepared from a combination of rubber, polychloroprene rubber, and acrylic latexes, blocked isocyanate, a hydrobrominated phenolic resin, and hexamethylene polysulfides [858].

A reusable, double face, adhesive sheet with high creep resistance has been patented. A polyester film that was primed on both sides was coated on one side with a hydroxy-functional polybutadiene and an MEKO blocked TDI/hydroxypolybutadiene adduct and on the other side with a butyl acrylate base adhesive [859].

6.5. Sealants

Sealants are materials that are used to fill gaps in joints such as between the glass and metal frame in a windshield, between two glass sheets in double pane glazing, in or over a metal joint and so on. Frequently they also act as an adhesive to hold two surfaces together as well as giving a smooth joint that does not leak.

A sealant for joining insulating glass using dodecyl mercaptan blocked isocyanate and a hydroxy-functional

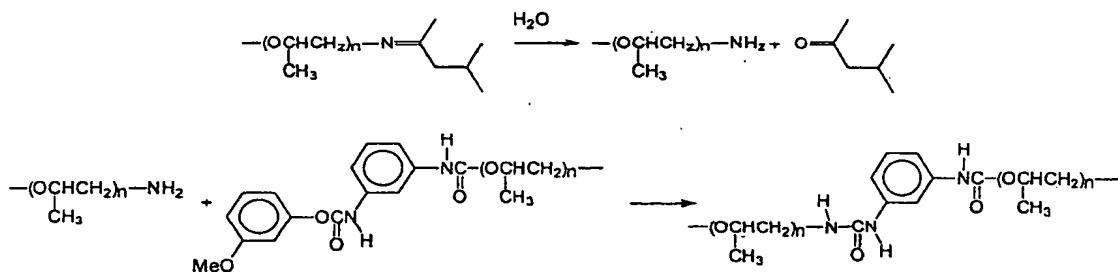


Fig. 17. Use of a blocked amine (ketimine) in curing 1K urethane sealants with a blocked TDI.

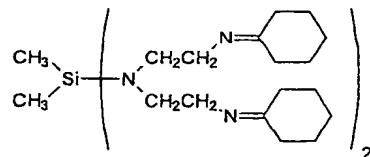
polybutadiene with the isostearic acid salt of ethylenediamine is stable for several weeks at 38°C and cures in less than 10 min at 150°C [860]. A glazing sealant is formulated with a *p*-hydroxybenzoate blocked prepolymer of MDI with polyether diol and triol using as a coreactant, a variety of hydroxy-functional materials or ketimine blocked polyamines [861]. A glazing sealant that cures by a combination of heat and moisture is formulated with an MDI prepolymer and a polyether triol with TDI uretdione, a trimethoxysilyl-functional acrylic resin, plasticizer, and a small amount of 4,4'-methylenebis(2-methylcyclohexylamine) [862].

A 2K sealant that cures in 30 min at 120°C is made with one package consisting of an MEKO blocked MDI/polypropyleneoxide diol and triol prepolymer and the second package is bis(4-aminocyclohexyl)methane [863]. Other 2K sealants are formulated with a nonylphenol blocked TDI/polyether triol and castor oil prepolymer in one package and polyethyleneoxide diamine and bisaminopropylpiperazine in the other package using DBU as a catalyst [864]. Thermal cure sealants are formulated with bis(4-aminophenyl)methane, an ethylene oxide-propylene oxide copolymer ethylenediamine adduct, an MEKO blocked TDI prepolymer with a polyether diol and triol, and MEKO blocked HDI polyether triol [865].

Use of a ketimine with a blocked isocyanate permits package stability in closed containers and curing after application when exposed to water vapor in the air. Reactive silanes are well known for enhancing adhesion to glass, addition of 0.2 parts of 3-glycidoxypropyltrimethoxysilane to isononylphenol blocked TDI polyetherpolyol prepolymer and MIBK ketimine of a polyether-polyamine sealant substantially increased the adhesion to glass [866]. A sealant containing 3-methoxyphenol blocked TDI polyether triol prepolymer, a ketimine derived from a polyoxypropylene diamine and MIBK (Fig. 17), and 3-aminopropyltriethoxysilane as an adhesion promoter showed excellent stability and cured after application [867]. A stable sealant is formulated with nonylphenol blocked TDI/polyether triol, hydroxy-functional silicone copolymer prepolymer with a ketimine from MIBK and a polyetherdiamine [868]. Use of polybutylene ether diol instead of polypropyleneoxide diol in the blocked isocyanate prepolymer cross-linked with a

bisketimine gives faster curing sealants [869]. IPDI blocked with 4-carbomethoxyphenol with a diketimine curative has faster cure and longer storage life than obtained with phenol or 4-nonylphenol blocked TDI [870]. The package stability of blocked isocyanate ketimine sealants is improved by adding a carbodiimide such as dicyclohexylcarbodiimide. For example, a carbodiimide is added to a sealant formulated with a nonylphenol blocked TDI/polyether polyol prepolymer with a ketimine from MIBK and a polyether diamine [871].

Moisture cure sealants prepared from a nonylphenol blocked IPDI/linear aliphatic hydroxy-terminated polycarbonate and a bisketiminosilazene derived from reacting 1 mol of DETA with 2 mol of cyclohexanone and 1 mol of dichlorodimethylsilane, use DBU as a catalyst [872]. A stable heat cured sealant is made with a nonylphenol blocked TDI polyether triol diol prepolymer, the bisketimine from IPDA and MIBK, and a water-releasing compound (the ammonium salt of the half di(2-hydroxyethyl)amine amide of phthalic acid) [873].



A bisketiminosilazene

A sealant that contains both epoxy groups and blocked isocyanate groups has been made by reacting a polyether diol and a methylol substituted BPA epoxy resin with MDI then blocking the residual NCO groups with MEKO and using an amino-amide from phthalic anhydride and DETA [874]. When the isocyanate unblocks it reacts with the amine groups as well as the epoxy reaction with the amine groups.

A 1K sealant for use over E-coated steel is made from a polyether triamine, polyether hexol and diol, TDI polyurethane with a paste of an encapsulated polyisocyanate in polyether polyol and polyether triamine [875]. The applied sealant was stable on exposure to humid air but cured at 120°C in 30 min. See Ref. [876] for the process for preparation of the encapsulated polyisocyanate.

Metal sealants cross-linked with blocked isocyanates are especially used in manufacturing automobiles; one group is thermosetting PVC plastisol sealants. Many patents covering chip resistant plastisol primers (see Section 5.4.2) state that the products can also be used as sealants. Calcium oxide has been added as one of the pigments in plastisol sealants to minimize blistering due to reaction with water at high humidity [877]. Mixtures of isopropylphenol and isoctylphenol have been used as blocking agents for TDI isocyanurate in a plastisol sealant [878]. A plastisol sealant using a xlenol blocked TDI prepolymer gave better storage stability and greater adhesion to E-coated steel after baking at 120°C for 30 min than a corresponding sealant with a nonylphenol blocked isocyanate [879]. A sealant based on nonylphenol blocked HDI-terminated polyurea with terminal amine groups and PVC is said to have improved adhesion and resistance to yellowing [880]. 2-Ethylhexyl *p*-hydroxybenzoate blocked TDI [881] and (α -methylbenzyl)phenol blocked TDI isocyanurate [882] increase the adhesion of plastisol sealants. Oxime blocked isocyanates have also been used [883]. Plasticizer free sealants are formulated with BPA epoxy resin, a phenol blocked polyisocyanate, and a modified polyamine. When used to seal automobile panels there was good yellowing prevention in both the base and topcoats [884]. Another plastisol sealant is formulated with 2EH 4-hydroxybenzoate blocked TDI isocyanurate with a tall oil BPA epoxy ester [885].

An automotive underbody sealant with at least 3-month storage stability and that cured in 20 min at 140°C has been patented using TDI uretdione particles as the “blocked” cross-linker for a polyhydrazide prepared by reacting an acrylic copolymer with hydrazine [886]. The particles are made by mixing TDI uretdione into a combination of polyether diol and triol at less than 35°C, then adding an amine-terminated polyamide at 20°C. The amine groups react with isocyanate groups on the surface of the uretdione particles to encapsulate them. Particles of urea encapsulated TDI uretdione in a polyether triol with a small amount of 2,5-dimethyl-2,5-hexanediamine are used with a polyether/polyester polyol to prepare underseal or door seals for automobiles [887]. A so-called PVC-free plastisol has been patented for sealing spot welds in automobile manufacturing. A dispersion of a butyl methacrylate/methyl methacrylate copolymer in dioctyl phthalate with an isononylphenol blocked polypropyleneoxide polyol and 4,4'-methylene-bis(2-methylcyclohexylamine) cured at 170°C in 20 min [888]. Another such sealer is made with poly(methyl methacrylate) powder dispersed in an MEKO blocked polyether triol compound [889].

2K waterborne sealants have been patented using an aqueous dispersion of a relatively high molecular weight polyether diol part of which was terminated with imidazole blocked TDI [6]. The sealant remains spreadable for 2 h after the dispersion of the blocked isocyanate is made.

Waterborne sealants with good alkali, blocking, efflorescence, and water resistance for cement and slate products

are formulated with a water-reducible acrylic resin and a blocked isocyanate [890].

7. Textile, paper, and leather applications

The characteristics required for textile, paper, and leather applications overlap. One of the common motivations for using blocked isocyanates in these applications is to replace formaldehyde-based treatments such as urea-formaldehyde resins.

7.1. Textile applications

Many different applications for blocked isocyanates in the textile field have been developed. Probably the first large scale commercial textile use was for bisulfite blocked isocyanate-terminated polyether polyols for treatment of woolen fabrics to give permanent crease properties. The fabric was treated, then fabricated into clothing, then at relatively higher temperature, pressing resulted in the final cross-linking so that the creases were permanent [891]. Wash fast, shrink-resistant treatment of wool fabrics so that wool fabrics can be cleaned by laundering rather than dry cleaning has been reported [892]. One such treatment consists of reacting part of the isocyanate groups of 2,4,4'-triisocyanatodiphenylether with stearyl alcohol and blocking the balance with sulfite groups [893]. An amphoteric polymer containing protonated amine and bisulfite blocked isocyanate groups has been used to shrink proof woolen fabrics [894]. An aqueous dispersion of a bisulfite blocked HDI polyether triol (molecular weight, 8000) prepolymer was used to shrink proof wool with softer hand [895]. Oil and water proofing of wool fabrics is done with a PUD from MDI, TMP, polyether polyols, and *N*-methyldiethanolamine blocked with MEKO [896].

Crease resistant treatments, particularly for cotton-polyester blend fabrics, have been the largest single use for formaldehyde containing finishes. Blocked H₁₂MDI and IPDI-terminated polyether polyol prepolymers emulsified in water give properties equivalent to dimethylol-dihydroxyethylene urea treatments [897]. An MEKO blocked TDI prepolymer that had been reacted with polyether polyols having sulfonate salt groups is recommended for crease proofing textiles [898]. A phenol blocked TDI derivative of hydroxypropylethoxylated lignin has been tested as a permanent press treatment of cotton [899]. A wash and wear fabric treatment is formulated with MEKO blocked H₁₂XDI TMP prepolymer and a PUD [900]. MEKO blocked water-dispersible polyurethane polyisocyanates are used for wash and wear treatment of cotton [901]. Cotton fabrics are treated for shrink proofing with waterborne blocked TDI/TMP and 1,4-butanediol prepolymer made by reacting part of the free isocyanate groups with taurine and the balance with phenol [37]. A dry cleaning resistant finish for cotton fabric is prepared from an acrylic latex from an MEKO

blocked TMXDI/TMP prepolymer reacted with HEMA and other acrylic monomers [81]. An anti-wrinkle treatment for cotton fabrics with reduced formaldehyde emission is based on replacing part of the usual urea-formaldehyde treatment with a DEM blocked H₁₂MDI-terminated polymer with a polyester polyol, a polypropylene glycol, and the sodium salt of a benzene sulfonic acid derivative of a bis(hydroxyethyl)ester of a phthalic acid [902]. A wash and wear, shrink proofing treatment for cotton fabrics is a PUD with terminal isocyanate groups blocked with MEKO [903].

Durable water and oil repellent and soiling resistant treatments for fabrics have been made to coat fabrics with fluorocarbon systems cross-linked with blocked isocyanates. ESCA analysis has been used to study the reactions taking place at the fabric surface treated with a fluorocarbon and blocked isocyanate to correlate reactions with the improved dry cleaning and wash resistance provided by the blocked isocyanate [904]. The cost of repellent treatments depends on the fluoro compound content. An extensive study of various approaches to minimizing required fluoro compound content is included in a patent [905]. Such variables as using fatty acid modified diols or siloxane diols in making the fluoro compound and use of octadecyl acrylate as one of the comonomers in preparing the latex component permit substantial reduction in cost without loss of performance properties.

A large number of patents have been issued covering various approaches to using blocked isocyanates in water and oil repellent treatments for textiles. Acrylic latexes including perfluoroacrylic ester and a monomer made by reacting HEA with IPDI [77] or MDI [906] and blocking the second isocyanate group with MEKO, or acetanilide half-blocked HDI [907] give water and oil repellent treated fabrics with excellent resistance to washing and dry cleaning. Use of a latex made from MEKO blocked IPDI adduct with HEMA, perfluoroalkylethyl acrylate, and a mono ester of a polyethylene glycol methacrylic acid has been patented [908]. An MEKO blocked water-dispersible polyisocyanate polyether prepolymer bearing sulfonate salts or a bisulfite blocked polyisocyanate polyether prepolymer bearing quaternary ammonium salts have been used with a perfluorinated acrylic resin to make oil and water repellent treatments that show excellent dirt resistance [24]. A water-dispersible bisulfite blocked polyisocyanate made by reacting HDI isocyanurate with a monoether of a polyether polyol and *N*-methyldiethanolamine and blocking with NaSO₃ is used with a perfluoroacrylic resin [909]. A cationic aqueous dispersion of a copolymer of perfluoroalkyl acrylic esters, vinylidene chloride, methylolacrylamide, acetone oxime blocked IEM, and 2-(trimethylammonium)ethyl methacrylate chloride gives an oil and water repellent treatment on polyester fabric with excellent wash fastness [910]. A water and oil repellent treatment for polyester fabrics uses MEKO blocked XDI with a perfluoroalkylethyl acrylate/di(6-hydroxyhexanoic acid)ethyl acrylate copolymer [911]. An aqueous emulsion of a BPA epoxy resin,

1,6-hexamidine and MEKO blocked TDI/TMP prepolymer with a fluoropolymer dispersion is used in a water and oil repellent treat for cotton fabrics [912]. An emulsion of MEKO blocked polyisocyanates and perfluorourethanes give particularly good dry cleaning resistance to oil and water repellent treated fabrics [913]. An emulsion of an *N*-methylperfluoroctylsufonamidylethyl acrylate (with 2-mercaptoethanol as chain transfer agent) MEKO blocked oligomeric MDI [914] or IPDI [915] adduct of HEMA with MEKO blocked HDI biuret/polyethylene glycol prepolymer gives an oil-water repellent finish with good wash fastness. An emulsion of an MEKO blocked adduct of polymeric MDI, an *N*-methylperfluoroctylsufonamidylethyl acrylate (with 2-mercaptoethanol as chain transfer agent), and polypropylene glycol is used as a water and oil repellent treatment for fabrics [916]. MEKO blocked HDI isocyanurate with acetone azine is used to cross-link a combination of a perfluoroacrylic resin made with *N*-methyl-*N*-perfluorooctanesulfonamidoethyl methacrylate, butyl acrylate, and *N*-ethyl-*N*-perfluorooctanesulfonyl glycine and a PUD made from a polyester diol, DMPA, TEA, and H₁₂MDI for a water and oil repellent treatment for textiles [917]. Further enhancement of water and oil repellent durability is reported using a combination of fluorocarbon and siloxane compounds. A copolymer of a perfluoroacrylic ester and a polysiloxane acrylic ester, and a hydroxy-functional monomer and MEKO blocked TMI is said to give superior retention of water and oil repellency after washing and dry cleaning than the corresponding polymer without the siloxane substituted monomer [918]. Polyamide fabrics are made water proof by first treating with a solution of sulfonated phenol-formaldehyde and then a perfluoroalkyl substituted acrylic copolymer and blocked isocyanate urethane prepolymer [919]. Nylon carpets are given a water-, oil-, and dirt-repellent treatment with a fluoroalkyl alcohol blocked HDI biuret emulsion and a perfluoroalkyl acrylic emulsion [920]. Anti-static water-repellent nylon fabrics are prepared by first treating with a polyoxyalkylene-polyurethane and then with a perfluoroalkyl substituted acrylic resin with a blocked isocyanate cross-linking agent [921]. Initial fibrillation of the surface of rayon fabrics before applying a fluorocarbon resin and blocked isocyanate treatment gives a fabric with very soft handle as well as good resistance properties [922]. Stainless steel metallized fabrics are treated with a fluoro-based repellent with a blocked isocyanate binder [923].

A treatment for dyed fabrics that gives excellent dry cleaning resistance for the color as well as very good oil and water repellency and that is fast to washing and dry cleaning has been patented [924]. MEKO blocked 2,2(4),4-trimethylene diisocyanate is used with a combination of perfluoroalkyl acrylate copolymers and a hydroxy-functional perfluoroalkyl urethane.

A soil proofing treatment for cotton-polyester fabrics was made from MEKO partially blocked HDI biuret with the other NCO groups reacted with a perfluoroalcohol and a

polypropylene glycol monomethylether; it is said that the isocyanates react with the textile fibers [925]. Oil and water repellent treatments are formulated with partially blocked TDI that is further reacted with a polyalkylene hexol and a perfluoroalcohol [926].

A washfast anti-static water-repellent treatment for nylon fabrics is based on fluoropolymers, blocked aliphatic isocyanate, and additives [927]. A water-dispersible resin prepared from HDI, polyols, DMAE, treated with diethylsulfate then blocking residual isocyanate groups with imidazoline is used for a anti-static treatment for nylon fabrics [928]. A water-soluble polymer from the reaction of ethylenediamine-propylene oxide-ethylene oxide reacted with HDI and blocked with sodium bisulfite is applied to a polyester suede fabric to give a fabric with good resilience, anti-static properties, and hygroscopicity [929]. An anti-static treatment for dyed polyester fabrics is made from an aqueous dispersion of a NaHSO_3 blocked HDI/polyetherpolyol prepolymer reacted with the product of reacting the same polyols with epichlorohydrin followed by reaction with DETA [930]. Another anti-static treatment consists of the reaction product of polyalkylene glycol diglycidyl ether, and sorbitol polyglycidyl ether with *N*-methyliminobis(propylamine)methosulfate was used to treat a polyester fabric, then the fabric was treated with sodium bisulfite blocked HDI/polyoxyalkylated ethylenediamine methosulfate and the fabric dried and cured [931]. A similar treatment of nylon fabric has been patented [932]. A durable anti-static treatment for polyester crepe fabric is a protein modified with a dextrin acrylic acid copolymer to give a functional protein and a bisulfite blocked HDI/polyether polyol [933]. Cotton fabric treated with an emulsion of a trimethylsilyl-terminated aminoethylaminopropylmethysilanediol-dimethylenesilanediol-methyloxirane-methylsilanediol-oxirane graft copolymer butyl ether and a blocked isocyanate showed good anti-static, softening, water absorption, and yellowing resistance [934]. A washable polyester fabric with good moisture absorption properties is obtained by treatment with a vinyl acetate/itaconic acid copolymer cross-linked with MEKO blocked MDI [935]. A similar treatment applied to nylon taffeta imparts durable anti-static properties [936]. Another anti-static treatment for nylon taffeta is formulated with NaHSO_3 blocked HDI with a polyester diol and a polyether diol [937].

Treating polyester fabrics with a bisulfite blocked isocyanate/prepolymer and heating gives a treated fabric with good hand and softness [938]. A soil and weather resistant fabric is made using a hydroxy-functional acrylic resin and MEKO blocked HDI polyisocyanurate [939]. An acrylic copolymer of MEKO blocked IEM, perfluoroalkylethyl methacrylate, and polyethylene glycol monomethyl ether methacrylate is used as an anti-soiling treatment for fabrics [940].

A wash resistant anti-bacterial treatment for cotton fabric is made from an aqueous emulsion of a polyether-

diamine reacted with MEKO blocked HDI incorporating 2,4,4'-trichloro-2'-hydroxydiphenyl ether [941]. An anti-bacterial and acaricidal treatment for polyester fibers uses a blocked isocyanate as a cross-linker for a styrene/acrylic copolymer [942]. Polyester fabrics are made fire resistant and anti-bacterial by coating with aqueous dispersions of an aminosaccharide, a blocked polyisocyanate, hexabromocyclododecane, and a bactericide [943]. Washfast, moth-resistant fabrics are made by applying isobornyl thiocyanatoacetate, a blocked isocyanate emulsion, and an aminosiloxane softener [944].

A cool touch fabric finish has been prepared from a blocked isocyanate emulsion containing a phthalocyanine compound. Near IR radiation is absorbed by a treated dyed cotton fabric so that it feels cooler in contact with skin than the untreated fabric [945].

Size coats for fibers have been patented; the largest number of patents cover sizes for glass fibers, these are discussed in Section 8.2. A size coat for synthetic fibers consists of a PUD made by reacting poly(butylene adipate), 1,4-cyclohexanedimethanol, and DMPA with excess TDI, blocking the residual isocyanate groups with butyl alcohol, neutralizing with TEA, and dispersing in water [946]. Sizing agents for polyester fibers are made with an amine/hydroxy-terminated polyester made with DMPA polyester, polyol, blocked isocyanates, and additives [31].

Aqueous dispersions of perfluoro polymers have been used with TDI uretdione to treat the surface of sewing thread to increase abrasion resistance [947]. Abrasion resistance of textile belts is improved without reducing flexibility by treating with a water dispersible blocked urethane prepolymer [948].

Blocked isocyanates have also been used in connection with coloring of fabrics. Polypropylene fibers have been treated with a coating based on blocked isocyanates that results in more easily dyed fabrics. A TDI-terminated polyether diol is blocked with MEKO and reacted with DETA followed by acetic and sulfuric acids that gives an aqueous salt solution for application to polypropylene fibers as a dyeing aid [949]. Treatment of dyed polyester/cotton fabrics to decrease wet and dry crocking (that is rubbing off of color) has been patented. An epoxidized polyamide, a CL blocked TDI/TMP polyether polyol prepolymer and a glyoxal resin was applied to dyed polyester–cotton fabrics, the resulting treated fabrics had much greater crock resistance than the untreated dyed fabric [950]. MEKO blocked TDI/TMP prepolymer is used with a hydroxy-functional perfluoroalkyl acrylic ester acrylic latex in a treatment for dyed nylon fabric that gives water-repellency and improves the wet crock resistance [951].

Blocked polyisocyanates have also been used as the cross-linker in pigmented textile print colors. MEKO blocked HDI isocyanurate that has been partially reacted with a monobutylether of a polyglycol and the sodium salt of 2-aminoethyl-2-aminopropionic acid is used as a cross-linker for a hydroxy-functional PUD with an acrylic

latex and with hydroxyethylcellulose as a thickener for a waterborne pigment print paste [26]. A dispersion of particles of TDI uretdione is made by milling a mix of solid TDI uretdione in paraffin oil with an amine-terminated polyamide. This is then used as a cross-linking additive to a textile pigment print paste whose principal binder is an acrylic latex that contains HEA and acrylamide as potential cross-linking sites. After printing a textile is cured at 140°C for 5 min, the printed fabric shows excellent wash and crock fastness [14]. Transfer printing of textiles is done with a dispersed dye containing ink with a polyether polyol and a blocked isocyanate, the dye is transferred by sublimation [952].

Plisse fabrics are manufactured by printing cotton fabrics with a print paste containing a water-soluble urethane, sodium bisulfite blocking agent, and a fluorocarbon waterproofing agent. After heat treating the printed fabric for 3 min at 160°C, the fabric is treated with sodium hydroxide solution, which shrinks the unprinted parts of the fabric. The result is a plisse fabric that is a fabric with rippled relatively transparent patterns [953].

Use of blocked isocyanates to cross-link binders for non-woven fabrics has been patented. Thus, an emulsion of MEKO blocked TDI/TMP with an acrylic latex having *N*-methylolacrylamide and acrylic acid as comonomers is used to impregnate a polyester non-woven web, cured 20 min at 160°C to give a bonded non-woven fabric with good bond strength [954]. A wide variety of methacrylic monomers with blocked isocyanate groups have been used as comonomers to make acrylic latexes for use as non-woven fabric binders [955]. For example, benzotriazole blocked TDI/HEMA adduct was used in making a latex with ethyl acrylate, it was used as a non-woven fabric binder with and without a diol such as 1,10-decanediol. Latexes made with MEKO blocked TMI, styrene, butadiene, acrylamide, HEA, and a small amount of divinylbenzene have been evaluated as non-woven fabric binders [75].

Deodorant treated fabrics are made by treating with a blocked isocyanate polyurethane formulation with added silica particles, which have been treated with (3-amino-propyl)triethoxysilane [956].

MEKO blocked TDI/TMP prepolymer and an acrylic resin has been used as the binder in flocked fabrics [957]. A water dispersion of a polyurethane/polyurea made with poly(tetramethylene glycol) and MDI chain extended with bis(4-aminophenyl)methane was used with blocked TDI as a binder for flocked fabrics [958]. See Section 9 for flock adhesives for flocked rubber.

Ornamental figures are thermally transferred to nylon fabrics using a phenol blocked MDI curing agent in a polyester polyol adhesive to assure good durability of the transfer ornament [959].

Wash resistant carpet backings containing blocked isocyanates as building blocks withstand 30 washings. Thus, an aqueous emulsion of MEKO blocked TDI/TMP prepolymer is emulsified into a carboxymethylcellulose solution

with a carboxylic acid-functional acrylonitrile/butadiene rubber latex and applied on a polyester/polyamide tufted carpet [960]. A similar backing that also includes an epoxy resin and MF resin to supplement the cross-linking by the blocked isocyanate has better pull resistance and somewhat better shrinkage resistance [961]. A non-curling, washable carpet backing uses an acrylonitrile/butadiene rubber latex, an aqueous dispersion of MEKO blocked HDI isocyanurate, MF resin, and a vulcanizing agent [961].

Aluminum-coated mesh fabrics useful for shading growing plants have been patented in which first a coating of MEKO blocked MDI is applied to a vinylon screen fabric, after drying and calendering at 130°C, an acrylic latex pigmented with leafing aluminum pigment is applied [962]. A binder for nylon fish net having long pot life, good adhesion, weather resistance, and peel strength has been patented is made with an MEKO blocked IPDI/prepolymer with polycaprolactone polyol and TMP mixed with a polyoxypropylene polyamine [963].

7.2. Paper applications

Several patents relate to various treatments for paper. As previously mentioned, a part of the rationale for using blocked isocyanate systems is to replace treatments involving formaldehyde derivatives. A cationic PUD prepared from polyethylene glycol, MEKO, a diisocyanate, and DETA is added to a paper pulp dispersion. Paper prepared using the dispersion cured 1 h at 102°C has improved dry and wet tensile strength as compared to a paper without the addition [964]. A styrene/butadiene latex including MEKO blocked TMI, and HEA as comonomers is applied to paper giving higher wet tear strength and lower yellowness index as compared to a paper treated with a styrene/butadiene latex made with *N*-methylolacrylamide as well as avoiding the presence of formaldehyde [73]. A bisulfite blocked HDI-terminated polyurethane based on poly(butylene adipate) and TMP gives a paper treatment that improves wet and dry strength [23]. A wet strength paper treatment consists of a copolymer of TMI blocked with 2-(trimethylammonium)ethyl alcohol sulfate with acrylamide and glyoxal [38]. Latexes made with MEKO blocked TMI, styrene, butadiene, acrylamide, HEA, and a small amount of divinylbenzene have been evaluated as paper coatings [75].

An ethyl alcohol blocked H₁₂MDI-terminated prepolymer with a polyester polyol and TMP is used to improve the dry and wet strength of thin tissue paper [965]. The strength of corrugated paper is improved by impregnating with an MEKO blocked TDI-terminated polyol-containing coating. After drying, the paper is heated to a paper temperature of 300°C under IR lamps [966]. Aziridine blocked MDI with an ethylene/vinyl acetate latex impregnated pulpboard is waterproofed after curing the dried pulpboard at 140°C for 30 min [967].

A latex made from MEKO blocked IPDI/HEMA, perfluoroalkyl acrylate, vinylidene chloride, and HEA is used to

impregnate paper to impart water and oil repellency [968]. A bisulfite blocked HDI-terminated silicone polyol is patented for use as a softening agent for paper [969].

A hydroxy-functional polyethylene/vinyl acetate latex, pigments, pentane encapsulated in microspheres, and MEKO blocked TDI/TMP prepolymer are coated on paper, dried, printed, expanded by heating, and embossed to give a high quality wallpaper [970]. A surface treatment for wallpaper is formulated with a blocked isocyanate, an acrylic resin, and a silicone resin or fluorinated polymer [971].

A high gloss coating for paper board is made with a thermoplastic cationic PUD made using an MEKO blocked TDI/polyether polyol which is reacted with a small excess of DETA and dispersing the product in aqueous acetic acid [89].

See Section 12 for discussion of synthetic or specially treated papers for printing and copying.

7.3. Leather applications

Blocked isocyanates have also found uses in the leather industry. Bisulfite blocked IPDI gave superior properties in tanning leather compared to bisulfite blocked HDI, presumably due to differential reactivity of the two isocyanate groups, and better color retention than bisulfite blocked TDI [972]. A tanning agent is prepared by reacting HDI with a small fraction of polypropylene glycol monomethyl ether and blocking with sodium bisulfite [973] or optionally also adding to this product a bisulfite blocked HDI isocyanurate and a polyether diol [974]. A biodegradable leather tanning treatment that is chrome-free yet still gives good properties includes a blocked isocyanate [975].

A laminate for coating split leather is made by first coating a release paper with a polycarbonate/polyurethane urea, applying intermediate coating layer of an MEKO blocked MDI and TDI-terminated urethane prepared from TMP polypropylene glycol ether and BPA polypropylene glycol ether prepolymer, bis(4-amino-3-methylcyclohexyl)methane, and pigment dispersions in dioctyl phthalate, and finally a urethane adhesive. The laminate is then applied to split leather [976]. Moisture permeable films for split leather or fabric are made by transferring a coating from a release paper topcoated first with a coating formulated with an anionic blocked isocyanate-functional PUD and bis(4-amino-3-methylcyclohexyl)methane and then with an adhesive coat of a similar PUD coating [977]. Porous coatings for leather are made using MEKO blocked PUDs with an amine and a water-reducible acrylic resin [978].

Several patents cover uses of blocked isocyanates in making synthetic leather. A PUD is prepared from a polyester diol, a polyol monoether, propoxylated 2-sulfo-1,4-butanediol sodium salt, IPDI, HDI, 75% DEM/ethyl acetoacetate blocked HDI isocyanurate, bis[2-(2-isopropyl-3-oxazolidinyl)ethyl]hexamethylenediacarbamate, hydrazine

hydrate, and water. A mixture of this dispersion, an aqueous dispersion of polyethylene, a polyester-siloxane, melamine resin, amine sulfonate catalyst, and a pigment paste was coated on release paper, dried and activated at 120°C, laminated on a polyester fabric and cured at 120–160°C to give a synthetic leather [979]. A similar solvent-borne procedure has also been patented [980]. Synthetic velour leather is made by coating both sides of a polyester fabric with an MEKO blocked MDI and TDI polyurethane formulated with polyol diols and triols, a hydroxy-functional polyester, 1,4-butanediol, bis(4-amino-3-methylcyclohexyl)methane, poly(butyl acrylate) and a dimethyl siloxane fluid, and finally embossing [981]. Yet another synthetic leather is made from MEKO blocked TDI/MDI/polyester diol and 1,4-butanediol and a blowing agent [982]. Another synthetic leather is made from phenol blocked TDI/poly(tetramethylene glycol) prepolymer, a condensation product of polypropylene glycol with hydroxylamine, blowing agent, and a pigment dispersion [983]. In another patent, a waterborne anionic PUD made with MEKO blocked MDI is used as an adhesive coating on a plastic topcoat that is subsequently transferred to a porous urethane coated fabric [17]. Synthetic leathers have been made by coating a topcoat of an emulsion of a polyurethane from an MEKO blocked MDI, TDI, propoxylated TMP, a polyethylene co-propyleneoxide diol, a hydroxy-functional polyester, and 1,4-butanediol thermally cross-linked after application to a release paper with bis(4-amino-3-methylcyclohexyl)methane followed by coating with a coating of an adhesive layer of an emulsion of a polyurethane from MEKO blocked MDI, TDI, propoxylated TMP and propoxylated BPA. The coated film was partially cured then laminated with fabric followed by final curing at higher temperature [61]. A suede leather substitute is made using a 2K system of MEKO blocked polyether polyol, polyester diol, 1,4-butanediol, MDI and TDI polymer and bis(4-amino-3-methylcyclohexyl)methane [984]. Another approach to synthetic leather is by molding a powder compound into a film. A CL blocked HDI-terminated polyester polyol, mixed low molecular weight diols derived polyurethane, is dispersed in water. A mixture of 1,6-hexanediamine and 2,2,4-trimethyl-1,6-hexanediamine is added, the resultant polyurethane-polyurea precipitates as a powder, which is subsequently molded into a film [985].

Adhesives for bonding synthetic leather products to a fabric substrate have also been patented. In one example, a layer of urethane synthetic leather on a release paper was coated with an adhesive based on MEKO blocked isocyanate-terminated polyester polyol was used as one package of a 2K adhesive in which the other package was dipropyleneetriamine. The film was then laminated to a textile backing sheet and cured at 140°C [986]. In another example, a fabric was coated with a cationic polyurethane dispersion mixed with a CL blocked MDI prepolymer then laminated to a poly(vinyl chloride)-based film to give an artificial leather [987].

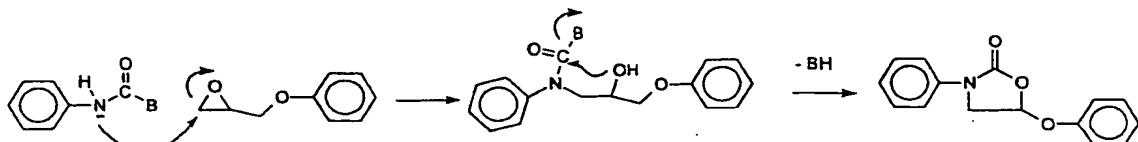


Fig. 18. Reaction of an aromatic isocyanate with an epoxy.

8. Plastics applications

Many plastics applications for blocked isocyanates have been studied. In addition to those discussed in this section, further applications are reported in Section 10.2 and coatings for plastics are discussed in Sections 5.4.1 and 5.6.

8.1. Molded plastics applications

8.1.1. Epoxy-based molded plastics

There are many applications for the use of blocked isocyanates with epoxy resins in molded products. As shown in Fig. 18, a blocked isocyanate can react directly with the epoxy group with subsequent cyclization to an oxazolidone; only aromatic isocyanates have a useful reaction rate. The oxazolidone structure gives the advantage of high thermal and chemical stability.

Use of mixed blocking agents, such as a combination of isononylphenol and DMP, to block TDI triol and diol prepolymers with BPA epoxy resin and bis(4-amino-3-methylcyclohexyl)methane have been patented [988]. Triphenylsilanol blocked TDI prepolymer is patented as a cross-linking agent for BPA epoxy resins [989]. An epoxy-functional 2,6-xylenol homopolymer, a graft copolymer of styrene and *t*-butyl alcohol blocked TMI, polypropylene, and a styrene/butadiene block copolymer gives molded pieces with higher impact strength and tensile elongation than without the graft copolymer [990]. Moisture absorption of epoxy–amine plastics made with tetraglycidyl-4,4'-diaminodiphenylmethane and 4,4'-diaminodiphenyl sulfone is significantly reduced by incorporating blocked isocyanates in the compound [991]. Lower moisture absorption was obtained using monofunctional compounds such as phenol blocked phenyl isocyanate and pentafluorophenol blocked cyclohexyl isocyanate, than difunctional ones such as phenol blocked HDI. The isocyanates reacted with amine groups and hydroxyl groups of the epoxy–amine polymer.

An MDI blocked isocyanate system for cross-linking epoxy resins has been patented in which the blocking agents evolved can further react eliminating the potential problem of the release of volatile blocking agents. 2-Benzoxazolone and 3,1-benzoxazine-2,4-dione react MDI to give blocked isocyanates. With epoxy resins these are stable at storage temperatures but at curing temperatures they release difunctional phenols as well as isocyanates [992]. The isocyanate reacts with epoxy resin to give oxazolidone cross-links. The

phenols react with epoxy groups and the isocyanates also react with the hydroxyl groups, which are generated through the reaction of phenol and epoxy groups as well as with epoxy groups (Fig. 19). Tetrabutylphosphonium acetate is used as a catalyst. No volatile compounds are emitted so the epoxy compound can be used in thick sections.

With some catalysts, lower cure temperatures can be achieved; however, a two package system is then required. For example, a compound formulated with an epoxy resin, phenol blocked MDI, and dimethyltin iodonium and tetraphenylantimony iodonium salts cures in 1 h at 130°C to give an oxazolidone cross-linked polymer with good heat resistance [993].

Many epoxy molding compounds are formulated with a combination of a blocked isocyanate and a polyamine coreactant. Spectroscopic studies of the reaction between tetraglycidyl-4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulfone, and *n*-butyl alcohol blocked HDI showed that in addition to the reaction of the amine with epoxy groups, reaction also occurred between isocyanate groups and amine groups as well as with the hydroxyl groups generated by the epoxy reaction [994]. As a result the equilibrium moisture absorption of the cured plastic is significantly reduced. The mechanism of the effect of blocked isocyanates on curing has been investigated using CL blocked TDI, HDI, and MDI with liquid BPA epoxy resin and polyoxypropylenediamine [995]. It was found that blocked aromatic isocyanates accelerated cure, whereas blocked HDI did not. It was found that not only do amine groups react with epoxy groups, but also the released isocyanate cross-links the hydroxyl groups of the reacted epoxy resin. As a result cross-link density and mechanical properties increase. The effect of molecular weight of nonylphenol blocked TDI/polyether diol prepolymers on the properties of amine/epoxy resin plastics has been studied [996]. The amine was shown to react with both the urethane and the epoxy resins giving a dual cross-link polymer. Low molecular weight prepolymers markedly increased impact properties but reduced flexural modulus and compression yield strength; higher molecular weight prepolymers slightly increased impact without changing other properties. Impact strength and heat resistance of piperidine cross-linked epoxy resins are increased by compounding with diethyl amine, phenol, or CL blocked TDI; physico-mechanical properties were studied [997].

TDI is reacted with 1-aminoethyl-2-methylimidazole and water to give a bisurea with the remaining NCO groups

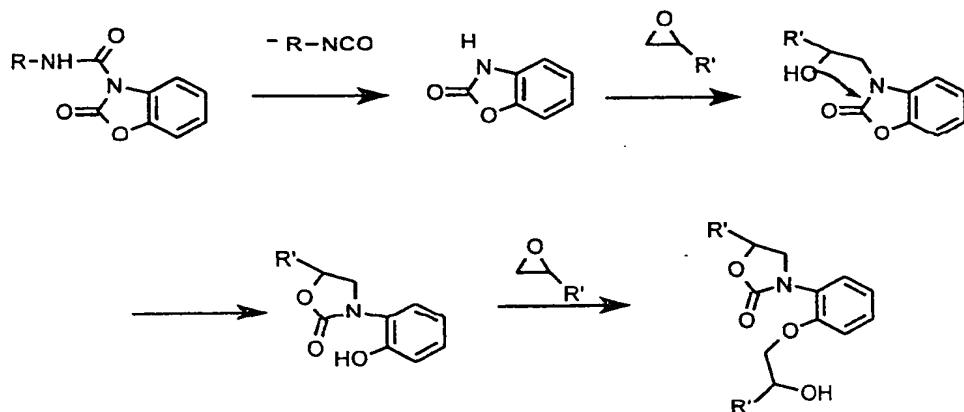


Fig. 19. Deblocking and subsequent reactions of 2-benzoxazolone.

blocked to give a catalyst for a storage stable compound of dicyandiamide and a BPA epoxy resin that cures in 6 s at 170°C [998].

Bicyclobetahydropyrimidines [209], imidazolines [999], and a mixture of 5,6-[(1-methyl-3-dimethyl)cyclopentano]-pyrimidine and 5,6-[(1-dimethyl-3-methyl)cyclopentano]-pyrimidine and their 2-phenyl derivatives [1000] are used to block an IPDI/diethylene glycol prepolymer. These are subsequently compounded with BPA epoxy resin and polyamine to give stable molding powders. Products are cured in a mold for 20 min at 180°C.

An isononylphenol blocked TDI/polyetherpolyol prepolymer, BPA epoxy resin, and 4,4'-methylenebis(2-methylcyclohexylamine) compound was molded at 180°C for 1 min [1001]. Improved properties, especially flexibility, are reported by using a mixture of blocking agents, such as isononylphenol and DMP with different deblocking temperatures, with polyether polyols to react with epoxy resin and 4,4'-methylenebis(2-aminomethylcyclohexylamine) [1002]. A nonylphenol blocked TDI polyoxypropylene oxide polyol, BPA epoxy resin, and amine-terminated triethylene glycol was poured into a mold and cured 2 weeks to give a molding with good impact resistance [1003]. IPDI blocked with 1-amino-2-(aminomethyl)-3,3(5),5-trimethylcyclopentane and a BPA epoxy resin is stable for over 24 h at 50°C and hardens to a smooth molding in 20 min at 180°C [1000]. A TDI or IPDI/polypropyleneoxide diol is blocked with nonylphenol and then reacted with *N*-aminoethyl-piperazine and trimethylhexamethylenediamine to give an amine-terminated polymer that is used with a BPA epoxy resin in a molding compound [1004].

One package epoxy–amine compounds have been formulated using fine particle size, solid imidazole blocked 1,5-naphthalenediisocyanate dispersed in a liquid BPA epoxy resin. During molding, the blocked isocyanate melts and deblocks; storage stability at ambient temperatures is 6–8 months and cure schedule is reported as 14 min at 85°C [1005].

Imide–siloxane prepolymers have been synthesized by reacting bis(succinylanhydrido-*n*-propyl)hexadecylmethylolsiloxane with imidazole blocked MDI [1006]. The prepolymers are to be used in modifying epoxy resins.

8.1.2. Urethane and urethane–urea compounds

Molded products made using a mixture of an ethylene/HEMA/methyl acrylate copolymer, polypropylene, and a CL blocked IPDI/ethylene glycol prepolymer have good oil resistance and tensile elongation [1007]. Acrylic urethane sheets are molded from an acrylic polyol and MEKO blocked H₁₂MDI [1008]. Another acrylic urethane sheet is cast with a polyurethane, an acrylic polyol, and CL blocked IPDI adduct as cross-linker [1009]. A blocked isocyanate-terminated oligomer made from MEKO half-blocked IPDI and diethanolamine is used with a hydroxy-terminated urethane to make thermoformable sheets [1010]. Elastomeric polyurethane moldings are made with TDI uretdione and polyetherpolyols using bismuth 2-ethylhexanoate with 2,4-diamino-3,5-diethyltoluene as a catalyst [1011].

A nonylphenol blocked TDI-terminated polypropylene glycol prepolymer combined with IPDA gives a polyurethane–urea plastic that cures at room temperature in 10 days [1012]. An isocyanate-terminated polyurethane from TDI and polyalkoxylated glycerol is blocked with a phenolic-containing hydrocarbon resin is cross-linked with IPDA using DBU as catalyst [1013]. The molding compound has the advantage that there is no volatile blocking agent. Polyurethane–urea moldings are also made with encapsulated particles (see Section 3.11) of TDI uretdione mixed with powdered solid polyamine coreactants [1014]. A “cold cure” 2K molding compound includes IPDI, polyether diamines, an encapsulated TDI uretdione powder with a pigment dispersion in polypropylene glycol. During 8 h at 50°C the isocyanate diffuses out of the particles giving a cured plastic [1015]. 2,2,6,6-Tetramethylpiperidine (and other similar amines) are used as blocking agents for IPDI-terminated polyoxypropylene glycol prepolymers as

one package and polyamines, such as pentaethylenehexamine, to make 2K molding compounds that cure at ambient temperatures [1016]. Similar 1K molding compounds can be made using ketimines. A 2K molding compound has as one package a paste containing TDI uretdione or MDI that has been surface reacted with amines or hydrazines and a second package of a polyol and/or a polyamine. The combined material is cast in a mold and heated to 150°C for 1 h and then tempered for an additional 4 h at 150°C [1017].

Blocked isocyanate-containing powders have been used in slush molding. A powder material is made which can be applied in a slush molding unit, fused to a continuous layer and then, with further heat, cross-linked. A powder from HDI uretdione with the free isocyanate groups blocked with *n*-octyl alcohol, a polyester polyol, and 1,4-butanediol has been patented [1018]. A polyurethane powder made from a PUD containing CL blocked IPDI isocyanurate is recommended for slush molding [1019]. A polycaprolactone diol prepolymer with IPDI, CL blocked IPDI isocyanurate, isophorone diamine and diethanolamine is used for slush molding parts for automobile interiors with little fogging of glass [1020]. A urethane elastomer and a blocked isocyanate are used as the vehicle for slush molded plastics [1021].

8.1.3. Polyamide, polyamide-polyimide, polyimide, and polyimide/epoxy compounds

It has been suggested that acetone oxime [150] and CL [1022] blocked IPDI isocyanurate are useful as cocatalysts for the anionic polymerization of caprolactam to nylon 6. Rapidly condensed polyamides are made with nylon 6 mixed with *N*-methylacetamide blocked MDI in the melt [1023]. Modified polyamides with improved impact resistance and elastic modulus are prepared by polymerizing CL in the presence of polyoxypiperylenediamine, and a mixture of CL blocked HDI and octadecylisocyanate [1024]. A nylon block copolymer with good impact resistance and tensile modulus is prepared by polymerizing CL in the presence of a CL blocked HDI-terminated polyether polyol [1025]. A nylon 6 polymer with incorporated liquid crystal blocks is made by reacting hydroquinone with terephthaloyl chloride, then reacting the product with HDI and blocking the excess isocyanate with CL and then adding further CL and polymerizing to form the polyamide polymer [1026]. Cross-linked nylon 1 films are prepared by homopolymerizing HDI and blocking the terminal groups with cresol then reacting with poly(hexamethylene adipate) diol [1027]. Polyamide films are made from poly(*p*-phenyleneterephthalamide) and CL blocked MDI [1028].

Polyamide-polyimide polymers are synthesized by the reaction of a diamine, trimellitic anhydride, and a blocked isocyanate. Polyamide-polyimides are more easily processed than polyimide plastics with good heat resistance although not as good as polyimides. Kinetic studies have been done on model compounds of reactions of *p*-chlorophenol

blocked phenyl isocyanate with phthalic anhydride and with benzoic acid [1029].

Rigid polyimides synthesized by reacting imidazole blocked 2,5-di-*n*-alkoxy-1,4-phenyldiisocyanate with pyromellitic dianhydride give layered structures with the layer spacing increasing as the alkyl chain is increased from 4 through 16 [1030]. Similar studies using imidazole blocked 2,5-((di-*n*-alkoxy)methyl)-1,4-phenyldiisocyanate [1031]. In a study of the effect of structure of imidazole blocking agent and polyisocyanate it is reported that the highest molecular weights are obtained using benzimidazole as the blocking agent and TDI as the diisocyanate reacted with pyromellitic dianhydride [1032]. Imidazole blocked 1,1'-disocyanato-2,5-bis(dodecyloxybenzene) reacted with pyromellitic anhydride gives polyimides with good processing characteristics but still not melting up to 400°C [1033].

Polyurethane-imide-oxazolidinone polymers have been synthesized [1034]. Phenol blocked TDI-terminated hydroxy-functional polybutadiene was reacted with diaminodiphenyl ether to yield a telechelic amine. This was then reacted with pyromellitic dianhydride to give a polyamic acid, which was cast in a mold and imidized by heating to 160°C.

8.1.4. Other molding compounds

Polyester plastics have been modified by use of blocked isocyanates. A blend of poly(ethylene terephthalate), core-shell butyl acrylate rubber grafted with methyl methacrylate, and CL blocked TDI prepolymer gave a molding with much higher impact strength compared to a molding without the blocked isocyanate [1035]. A mixture of an ethylene glycol/neopentyl glycol/terephthalic acid polyester was blended with a CL blocked isocyanate. Electrostatically charged particles of a powder were applied to a conveyor belt and heat rolled at 190°C to give resin sheets [1036]. Poly(butylene terephthalate) is stabilized against thermal degradation during processing by addition of BPA epoxy resin and CL blocked IPDI [1037]. MEKO blocked HDI/polyester polyol prepolymer and a polyester polyol are press formed to give a transparent film [1038].

Potential problems caused by release of a volatile blocking agent during molding can be avoided by use of a blocking agent that becomes chemically bonded during cure. For example, use of benzylmethacrylohydroxamate blocked MDI in an unsaturated polyester molding compound gives moldings with higher tensile and impact strengths [1039].

The mechanical properties of an MEKO blocked IPDI cross-linked PVC-hydroxy-functional acrylic polymer blend are compared with a similarly cross-linked PVC to which a hydroxy-functional acrylic has been grafted as well as other cross-linked polymers [1040]. PVC molding powders prepared using a mix of PVC resin and hydroxy-functional PVC resin, a polyester polyol, and a blocked aliphatic isocyanate give molded products with good compression set and tensile strength [1041].

High density polyethylene functionalized by graft polymerization of CL blocked half adduct of IPDI and HEMA gives a polymer that after processing has a higher tensile strength than the unmodified polyethylene [1042].

Phenolic/hexaminetetramine molding compounds with good molding and curing properties are obtained by incorporating xylenol blocked polymeric MDI [1043].

Molding compounds of polyoxymethylene reacted with blocked MDI have good mechanical properties without fiber reinforcement [1044].

Weld strengths and impact resistance of polyphenylene sulfide moldings are increased by adding a blocked polyisocyanate and a maleated ethylene copolymer [1045].

Silica filler surfaces treated with HDI followed by over-coating with methyl alcohol blocked HDI in polycarbonate plastics give molded plastics with improved mechanical properties [1046].

A UV cure composition for film for three-dimensional moldings is formulated with ethyl alcohol blocked TDI/HEA adduct, HEA esters derived from alkyl polycarbonates, *N*-vinylcaprolactam, and isobornyl acrylate [1047]. The film is molded and then thermally cured.

8.2. Reinforced plastics applications

Several patents have been issued covering use of blocked isocyanates in sizes for glass fibers for use in reinforced plastics. Sizing increases the abrasion resistance of the fibers and improves the adhesion, particularly in the presence of water between the fiber and the plastic. A CL blocked H₁₂MDI PUD, a thermoplastic PUD, and 3-aminopropyltriethoxysilane is used to size glass fibers used in reinforcing polyamide plastics [1048]. Fiber glass sizes formulated with an MEKO blocked water-dispersible polyisocyanate prepared from HDI biuret and a monobutyl ether of polyethylene glycol have been used to reinforce nylon 6 plastics [1049]. A blocked PUD, aqueous dispersion of an epoxy resin, DETA methylisobutyl ketimine, and an aminosilane are used to treat glass fiber for reinforcing thermoplastic polymers such as poly(butylene terephthalate) and poly(phenylene oxide) [1050]. An MEKO blocked HDI PUD with an aqueous dispersed epoxy resin is used as a size for glass fibers [1051]. CL blocked 3-isocyanatopropyltriethoxysilane has been patented for use as a size for glass fiber to be used in laminating nylon 66 films [1052]. Glass fiber sized with an MEKO blocked PUD and an amino reactive silane are used to reinforce polyoxymethylene plastics [1053]. An MEKO blocked TDI PUD size for glass fibers is used to reinforce polyethylene and polyester plastics [1054]. Blocked isocyanate sized glass fibers give higher strength moldings than with other size coats when used to reinforce an alternating CO, ethylene, propylene copolymer (a polyketone resin) [1055]. Sizes containing blocked isocyanates for carbon fibers used in polycarbonate plastics have also been patented [1056]. A variety of blocked isocyanates including CL blocked

HDI have been patented for use as carbon fiber sizes [1057].

Blocked isocyanates have been used in many types of glass and carbon fiber reinforced plastic molding compounds and preprints. Addition to a styrene-unsaturated polyester of isononylphenol blocked TDI isocyanurate and a polyol gives a molding with increased flexural modulus and strength [1058]. A small addition of imidazole blocked isocyanate to a brominated epoxy/phenolic resin blend and phenol-modified polybutadiene prepreg gave pressed boards with good machinability and dimensional stability [1059].

Prepregs with improved storage stability are made by using a blocked isocyanate, 2-ethyl-4-methylimidazole and dimethylamine blocked IPDI, as a latent catalyst [1060]. Prepregs made with epoxy resin, epoxy acrylate, and CL blocked HEA are made by vacuum impregnation followed by UV curing to B stage [1061]. Moisture absorption by epoxy resin graphite fiber composites is reduced by including blocked isocyanate in the compound [1062]. Impregnated epoxy glass patches including imidazole blocked naphthalene diisocyanate give improved performance [1063].

Glass fiber reinforced polyurethane plastics are prepared using polyols with a combination of MDI and phenol blocked HDI [1064]. A prepreg with an MEKO blocked TDI prepolymer with IPDA gave a stable prepreg, which cured with a lower exotherm than epoxy preprints [1065]. MEKO blocked diisocyanates in polyurethane-polyether preprints give 20–40°C lower cure temperatures than obtained with CL blocking [1066]. Use of diacetone acrylamide oxime as a polymerizable blocking agent was also studied for molding thick pieces [1066].

Pultruded polyurethane glass, carbon, and aramid fiber products have been studied using a CL blocked TDI/branched polyester polyol with bis(3-amino-4-methylcyclohexyl)methane [1067]. Phenol blocked TDI-terminated polyol is added to a phenolic compound for pultrusion with glass fiber increasing toughness and coupling to the glass fiber [1068]. The reactions and mechanical properties of a pultruded glass fiber reinforced CL blocked TDI polyester prepolymer, resole phenolic resin, dipropylene glycol compound with pTSA catalyst have been studied [1069]. It was shown that isocyanate group reacted with the phenolic hydroxyl groups improving the toughness of the product.

Phenol blocked TDI isocyanurate is used with a polyetherimide for making prepreg for laminates that have good high-temperature resistance properties [1070]. CL blocked TDI polyol prepolymer improves the impact resistance of poly(ethylene terephthalate) glass fiber reinforced moldings [1071]. Phenol blocked TDI-terminated polyol is used in making polyether plastic glass reinforced molding [1072]. Oxime blocked HDI increases the flexural strength and modulus of glass reinforced polypropylene sheets [1073]. Preprint sheets of polyester and carbon fiber non-woven fabric are coated with a thermosetting acrylic resin with a blocked isocyanate cross-linker to make a sheet for

laminated moldings [1074]. Use of water-soluble bisulfite blocked TMXDI has been patented for treating jute fibers for use as reinforcing fibers in phenolic and urea-melamine high pressure laminates [22]. Water-resistant sheets are prepared by treating pretreated straw with an emulsion of paraffin and laurolactam blocked MDI [1075]. Decorative paper is impregnated with an MF resin and an MEKO blocked isocyanate and pressed on a phenolic resin core [1076].

High temperature resistant laminates of steel and titanium are made using polyimide plastic from phenoxyethyl alcohol blocked MDI isocyanurate with the condensation product from 3,3'-diaminobenzophenone and 3,3',4,4'-benzophenone tetracarboxylic acid reinforced with glass fabric [1077].

8.3. Coated fabrics applications

Textile coatings that result in products that retain their textile form are covered in Section 7.1, in this section, we cover plastics that have a supporting textile substrate. Typically such products are vinyl coated fabrics that are usually considered part of the plastics field. In many cases similar products are used to make leather coatings or synthetic leathers (see Section 7.3).

Fabric is coated with a 2-ethylhexyl 4-hydroxybenzoate blocked TDI isocyanurate-containing plastisol to obtain a coated fabric with good adhesion to the fabric [1078]. Cotton fabric is first coated with an MEKO blocked MDI and TDI-terminated urethane prepared from TMP polypropylene glycol ether, BPA polypropylene glycol ether, using 4,4'-methylenebis(3-methylcyclohexylamine) as a cross-linker. The pretreated fabric is then topcoated with an MEKO blocked MDI and TDI-terminated urethane from a polyester diol and 1,4-butane diol, using 4,4'-methylenebis(3-methylcyclohexylamine) as cross-linker [1079,1080]. A moisture permeable coating is formulated with an MEKO blocked TDI/polyether polyurethane with bis(4-amino-3-methylcyclohexyl)methane [1081]. Water-permeable coated fabrics are made by laminating a fabric with a film prepared from an MEKO blocked MDI, TDI prepolymer with a combination of polyether diols and triols with the NaHSO₃ adduct of butenediol cross-linked with bis(4-amino-3-methylcyclohexyl)methane [1082]. A release paper was coated with a pigmented polyester-polyurethane and then coated with a primer containing an MEKO blocked MDI-terminated urethane from polyether polyols and a polyester polyol using 4,4'-methylene-bis(2-methylcyclohexylamine) as a cross-linker, then laminated with a fabric and cured [1083]. A fabric is coated with a polyester/polyurethane and a blocked isocyanate in dimethyl formamide, treated with coagulating solution, washed, treated with silicone waterproofing agent then finally heat cured to give a soft water-resistant coated fabric [1084]. There is also a patent covering a similar process without the coagulation step [1085].

Non-yellowing polyurethane coated fabrics have been prepared by coating a release paper with an MEKO blocked H₁₂MDI prepolymer from a hydroxy-functional biscarbamate and a hydroxy-functional ester from caprolactone with 1,6-hexanediol and diphenyl carbonate and bis(4-amino-3-methylcyclohexyl)methane, heating 5 min at 160°C. The laminate is then coated with an adhesive layer comprised of an MEKO blocked MDI- and TDI-capped polyether triol with bis(4-amino-3-methylcyclohexyl)methane and laminating to cotton fabric followed by curing 3 min at 160°C [1086]. A urethane coated fabric is made by coating a release paper with a solvent-borne topcoat formulated with a polyurethane, then coating with an adhesive formulated with an MEKO blocked PUD, a methylolacrylamide-functional acrylic resin, and MF resin, then laminating to a fabric [1087].

Fabrics for tarps are made by impregnating polyester fabric with a PUD, a blocked isocyanate, and a fluoro-waterproofing agent and then topcoating with a polyurethane [1088]. A woven fabric of aramid fiber was treated with a waterborne coating containing a urethane emulsion and an aqueous dispersion of CL blocked MDI, dried, heat-treated 1 min at 190°C, coated with a PVC plastisol and heat-treated at 190°C to give a coated fabric with excellent bonding of the fibers to PVC [1089]. A fabric with a silk-like feel is made by coating a dyed, waterproofed nylon taffeta with a polyurethane elastomer, blocked isocyanate, treated with coagulating solution and dried. It is then coated with a waterborne coating of a fibroin-acrylic acid sodium salt graft copolymer and blocked isocyanate [1090].

A vinyl sheet containing, in addition to conventional components, a minor amount of a cross-linkable vinyl resin and a blocked isocyanate is laminated with an adhesive to cloth and then used to line a mold (cloth side out) for ABS injection [1091]. A release paper was coated with a pigmented polyester/polyurethane topcoat, then coated with a primer containing a polyurethane, MF resin, and DEM/ethyl acetoacetate blocked HDI isocyanurate and laminated to polyester fabric [1092].

A pipe repair coated fabric is a laminate of cloth with two layers of polyurethane coatings made with blocked isocyanates, one a flexible layer and the other a stretchable gas and liquid impermeable, pore free layer [1093].

A mixed amine-terminated silicone elastomer and hydroxy-terminated silicone fluid with combustion inhibitors containing a small amount of ethyl acetoacetate blocked IPDI isocyanurate is applied to glass fiber cloth [1094].

A foam-coated fabric is made with a hydroxy-functional acrylic latex and encapsulated TDI particles as a blocked isocyanate, foamed with air and dried at 150°C [1095]. A water-permeable foam coated fabric is made by applying a topcoat formulated with an MEKO blocked MDI and TDI/polyether prepolymer with bis(4-amino-3-methylcyclohexyl)methane. A foamable coating of similar composition with an added blowing agent, and a similar adhesive coating

are applied successively on release paper then the coating is laminated to a fabric and cured [1096].

8.4. Foam plastics

Thermoformable flexible polyurethane foams are prepared by incorporating blocked isocyanates into the foam compound [1097]. Thermoformable rigid polyurethane foams are prepared by incorporating CL/nonylphenol blocked polymeric MDI in a polyurethane foam composition [1098]. Vinyl chloride foams are prepared with PVC, hydroxy-functional acrylate/vinyl chloride copolymers and blocked isocyanates [1099]. Another in-mold surface coating is made with polyol diamines and encapsulated TDI particles. It is applied to the inside of a hot mold and then a rigid urethane foam is formed in the mold [1100]. An in-mold coating of a linear polyurethane and a blocked isocyanate is applied to a mold and then a urethane foam compound is back filled to yield a foam molding with a flexible tough skin [1101]. A blocked TDI polyurethane coating is applied to the surface of rigid polyurethane foam [1102]. A plastic film is coated with a carboxylic acid-functional acrylic resin with CL blocked TDI and after curing is used as a liner in a mold to fill with urethane foam [1103].

Molded foam products have been prepared by slush molding a skin with a powder made from an HDI polyester diol prepolymer, ethyl 4-hydroxybenzoate blocked of a prepolymer made by reacting excess HDI isocyanurate with a polyester diol and a pigmented polyester diol, and 1,4-butanediol in a non-solvent, filtered, and dried, followed by filling the mold with a similar unpigmented powder containing a blowing agent [1104].

Addition of a blowing agent to an 80% hydrolyzed ethylene/vinyl acetate copolymer containing CL blocked MDI gives a powder coating that yields a cellular foam coating for foam-in-place thermal insulating coating of pipes or boxes [1105].

A polyether-polyurethane foam sheet is impregnated with a solution of phenol blocked MDI and laminated with a polyester non-woven fabric to make a sound insulating decorative interior fabric for interiors of automobiles [1106]. Heat moldable foam sheets are made by foaming a polyurethane compound containing ethyl acetoacetate blocked HDI biuret between two layers of PET film treated with release agent and setting in a mold at 180°C for 10 min [1107].

A hydrophilic porous film is made from a blend of a graft copolymer of HEMA and methyl methacrylate on polyN-vinylpyrrolidone, a polyether polyol and a blocked isocyanate by coating the mixture on a greased aluminum panel, curing, and immersing in water [1108].

9. Rubber applications

Ref. [1109] reviews three approaches to cross-linking diene rubbers that involve isocyanates (1) reaction of a

rubber with active hydrogen substituents with a polyisocyanate, (2) reaction of an blocked isocyanate-functional rubber with a polyol, and (3) use of rubbers having both types of substituents on the rubber molecules. CL blocked TMI is copolymerized with butadiene and acrylonitrile and vulcanized with tetramethylene glycol by curing 30 min at 175°C [1110–1112]. Pyrrolidone blocked TMI has a high deblocking temperature, deblocking only starts at about 160°C. This is desirable since it minimizes scorching during processing prior to vulcanization [1113]. Acrylonitrile butadiene or styrene butadiene rubbers with pyrrolidone blocked TMI and hydroxypropyl methacrylate comonomers are vulcanizable with heat [1112]. Two acrylonitrile butadiene rubbers, one of which uses pyrrolidone blocked [1111] or CL [1114] TMI as a comonomer and the other has HEMA as a comonomer cross-link with heat. CL blocked TMXDI has been used as a cross-linker for styrene butadiene HEMA rubber [1114] or acrylonitrile butadiene HEMA rubbers [1111]. Modification of chlorinated butyl rubber with dibutylamine blocked TDI isocyanurate enhances the physico-mechanical properties of vulcanizates [1115]. CL blocked TDI as a modifier for rubber increases durability and resistance to heat build-up as compared to conventional tires [1116].

Urethane elastomer compounds have the distinct advantage that they can be liquids, which can be cast in molds and then cured. For electrical insulation, urethane elastomers based on hydroxy-terminated hydrogenated polyolefin polyol and a series of phenol blocked MDIs were evaluated. The phenol (phenol, nonylphenol, or long chain alkylphenols) used for blocking had only moderate effects on mechanical properties but the electrical insulating properties increased greatly with increase of the alkyl chain length in the phenol [1117]. Polyurethane moldings with faster demolding times are obtained with a phenolic resin blocked MDI-terminated polyol prepolymer than without the phenolic resin [1118]. A pourable, stable, vulcanizable polyurethane elastomer is prepared from a hydroxy-terminated urethane prepolymer and MEKO blocked polymeric MDI which was poured into a mold and rapidly mixed with 1,4-butanediol at 100°C and aged 24 h before demolding [1119]. A mixture of hydrogenated polyisoprene diol, MEKO blocked TDI and 1,4-butanediol gives a liquid compound with good storage stability and weather-resistant cured products [1120]. Acrylic elastomer stock made from a hydroxy-functional acrylic resin and CL blocked IPDI is stable 14 days before vulcanization and vulcanizes in 10 min at 180°C [1121]. An acrylic elastomer with improved scorch resistance is compounded with an acrylic elastomer, CL blocked HDI isocyanurate, and di-*o*-tolyl guanidine [1122]. Rubber products with high tensile strength are made with CL blocked TMI/acrylonitrile/butadiene/hydroxypropyl methacrylate/*N*-(4-anilinophenyl)methacrylamide copolymers with plasma treated aramid fiber reinforcement [1123]. It is suggested that the blocked isocyanate may, in addition

to cross-linking the rubber, also react with the surface of the plasma treated fibers.

Urethane elastomers that cure in 30 min at 130°C are prepared from an emulsion of MEKO blocked TDI tetramethyleneether glycol and bis(4-aminophenyl)methane [9]. Molded urethane elastomers are prepared from encapsulated particles (see Section 3.11) of TDI/polyol prepolymer surface stabilized with diamine and 1,4-bis(2-(4-aminophenoxy)ethoxy)benzene [1124].

For many years, blocked isocyanates have been incorporated into rubber compounds. More usually they are used to treat fibers to enhance adhesion between the rubber and the fiber, e.g., tire cord. A study is available comparing the effect of various tire cord adhesives and fibers (nylon 66, polyester, and aramid) with both natural and synthetic rubber [1125]. Possible mechanisms of adhesion of coatings to fiber and of modified fiber to rubber with different fibers are discussed [1126].

PET fiber is treated with a first coat of BPA epoxy resin, blocked isocyanate, and rubber latex and then as a second coat a mixture of resorcinol-formaldehyde resin and a butadiene/styrene/vinylpyridine latex; there are several variations of the treatments [1127]. PET fibers have also been first treated with polyethyleneimine solution and then with a mixture of vinyl pyridine rubber latex, resorcinol-formaldehyde, and CL blocked MDI [1128]. Polyester fibers are treated with polyethyleneimine, then with a blocked isocyanate, and finally with resorcinol-formaldehyde latex [1129]. A polyallylamine polymer and a blocked isocyanate are used to treat polyester fiber to provide good adhesion to rubber [1130]. Aqueous binder dispersions for treating aramid fibers using blocked isocyanates with a 2,3-dichloro-1,3-butadiene/vinylbenzylchloride/acrylic acid latex have been patented [1131]. Waterborne MEKO blocked MDI/polyester polyol/1,2-propanediol-3-dimethylamine polyurethane was used to treat aramid cords, which were then treated with a resorcinol-formaldehyde dispersion to give cords with high fatigue life and good adhesion to rubber [1132]. Polyester or aramid fibers are treated with a *p*-chlorophenol/resorcinol formaldehyde resin, and aqueous PTFE dispersion and a blocked isocyanate [1133]. A nitrile rubber latex containing pyrrolidone-blocked TMI comonomer and Kevlar® fiber that had been plasma treated with ammonia showed greater tensile and elongation at break than without the plasma treatment [1134]. Nylon 66 cord is treated with an aqueous dispersion of resorcinol-formaldehyde resin, a chloroprene latex, and a blocked isocyanate for use in reinforcing chloroprene rubber products [1135]. Nylon 6 cords are treated with a water-soluble phenol blocked HDI-terminated urethane from a hydroxy-terminated 1,6-hexanediol/maleic anhydride polyester that was reacted with TMP and sodium bisulfite and sodium sulfite followed by a resorcinol-formaldehyde and rubber latex coating [1136]. Polyester fibers are treated with glycerol polyglycidyl ether and MEKO blocked HDI then twisted into cords that are then dipped into a

resorcinol-formaldehyde latex, a chloroprene rubber latex, an ammonium salt of glycerol polyglycidyl ether and used in laminated chloroprene rubber sheets [1137]. Nylon 6 tire fabric for reinforcing (semi)transparent rubbers are colored and bonded simultaneously with a phenol blocked isocyanate containing treatment that also includes a red pigment [1138]. A liquid crystal polyester fiber is treated with a blocked isocyanate [1139].

An alkyl phenol made by alkylation with C₂₀–C₂₈ α-olefin is used to block MDI, which is used with hydrogenated hydroxy-functional rubber, and an EPDM rubber solution to make an adhesive for vulcanized rubber superior to EPDM rubber alone [1140]. Tapes for rubber shoe rims are coated with an adhesive composed of rubber, blocked isocyanate-terminated polybutadiene, and additives [1141]. A rubber-based shoe adhesive made with a combination of natural rubber and hydroxy-terminated polybutadiene is compounded with a second package containing a phenol blocked polyisocyanate, has a pot life of 2 weeks and cures at 125–130°C [1142]. A primer for vulcanized EPDM sheets made with blocked MDI and hydroxy-terminated hydrogenated polybutadiene, which was then coated with a BPA epoxy adhesive and bonded to steel had enhanced peel strength as compared to a system without the primer [1143]. Adhesives for bonding metal to rubber highly filled with carbon black are formulated with blocked isocyanate-containing adhesives [1144].

Paper impregnated rubber gasketing is manufactured by beater addition of a self-curing latex having pendant CL blocked isocyanate groups copolymerized in the latex by using TMI as a comonomer with a water-insoluble hydroxy-functional compound [76].

Extruded weather stripping is made with a blocked isocyanate-functional polybutadiene, norbornene rubber, and EPDM rubber [1145]. Coatings for EPDM rubber glass run channels are made using CL blocked MDI/hydroxy-terminated polybutadiene prepolymer and 2-ethyl-2-hydroxymethyl-1,3-propanediol [1146] and MEKO blocked MDI with a hydroxy-terminated polyester [1147]. Abrasion resistant, low friction coatings for rubber glass run channels are formulated with an MEKO blocked polyisocyanate polybutyleneoxide polyol prepolymer with a combination of polyethylene and polytetrafluoroethylene powder [1148]. Other coatings for glass channels with reduced friction are made with MEKO blocked MDI prepolymer with hydroxy-terminated hydrogenated polybutadiene and MEKO blocked MDI prepolymer with perfluoropolyoxetanes [1149] and an MEKO blocked polymeric MDI prepolymer of heptafluorobutanol and polyethylene glycol with a polyethyleneoxidetriamine [1150].

EPDM rubber sheeting with a flocked fiber surface is made using a flock adhesive prepared with nonylphenol blocked polyether polyol prepolymer, dinitrosobenzene, and a novolak epoxy resin [1151]. Attaining good flock adhesion requires use of a phenol blocked isocyanate; MEKO blocked isocyanates do not give as good properties. Lami-

nated materials for wearing apparel are made by laminating a polyester fabric treated with a fluorinated acrylic resin and a blocked isocyanate onto a chloroprene rubber cellular sheet [1152].

TMI is blocked with various chemicals that are anti-degradants for rubber [1153]. The blocked monomers can be copolymerized to make styrene/butadiene and acrylonitrile/butadiene copolymer rubbers that have anti-oxidant, anti-ozonate, synergists, plasticizers, cure activators, accelerators, and retarders as pendant side chains on the rubber molecules. For example, 2,2'-methylenebis(4-methyl-6-*t*-butylphenol) blocked TMI copolymerized in an SBR rubber reduces oxygen uptake to a greater extent than a control rubber. Similar results have been reported with isocyanate-functional rubbers made by copolymerizing styrene and butadiene with unblocked TMI and then reacting part of the isocyanate groups with anti-degradants such as anti-oxidants [1154].

Vibration damping materials with low temperature flexibility are prepared with hydroxy-terminated polybutadiene, hydroxy-terminated polysiloxanes, asphalt, and a blocked isocyanate [1155].

10. Electrical and electronic applications

10.1. Conductive adhesives and compounds

Electroconductive adhesives are made with a blocked isocyanate-terminated urethane prepolymer, a hydroxy-terminated polybutadiene and powdered copper [1156] or from BPA epoxy-urethane-based blocked isocyanate, hydroxy-terminated polybutadiene and flake silver powder [1157], or with an epoxy resin and CL blocked TDI isocyanurate and silver flakes [1158]. An anisotropically electroconductive adhesive is formulated with phenol blocked TDI, a polyester polyol, a thermoplastic polyester adhesive, and tungsten carbide powder [1159]. Conductive adhesives with reduced semiconductor warpage are made with phenol blocked isocyanate/hydroxy-terminated polybutadiene prepolymer, hydroxy-terminated polybutadiene, water repellent, and silver powder [1160]. A variety of blocked isocyanates and polyol compositions made conductive with silver flake have been patented for use as coatings, silk screen printing inks, and adhesives for circuit boards [1161]. Similar compositions formulated with poly(*p*-hydroxystyrene), MEKO blocked HDI isocyanurate, and a high HMMM MF resin has been patented [1162]. Silver–copper alloy is used as a pigment in a DEM blocked HDI isocyanurate compound printed on a substrate to make a circuit board with high electrical conductivity and good adhesion [1163]. Conductive coatings are made with mixtures of carbon blacks and graphite pigmented phenol blocked TDI/TMP prepolymer polyester–polyurethane formulations [1164] and with silver powder [1165] or scaly carbon black, polyester polyol, and imidazole blocked HDI TMP prepolymer [1166]. Soldering

paste containing phenol blocked HDI deactivates acid thus preventing corrosion of copper in printed circuit boards [1167].

A conducting coating of polyvinyl alcohol and blocked isocyanates is used to make a dewing sensor [1168].

10.2. Coatings and adhesives for use in electronic applications

A storage stable adhesive containing a polyester polyol, epoxy resin, and MEKO blocked HDI isocyanurate with salts of 1,8-diazabicyclo[5.4.0]undecene-7 is used to laminate a polyester film to a flexible copper-clad laminated board [1169].

Laminates useful for electronic wiring boards are made using fiber glass cloths surface treated with amino alkoxysilane coupling agents and blocked MDI [1170]. An aramid non-woven fabric is prepared using an epoxy resin emulsion and a blocked isocyanate as the binder [1171]. Films prepared from a hydroxy-terminated polyester from ethylene glycol, neopentyl glycol, and terephthalic acid with a CL blocked isocyanate are useful in flexible printed circuit boards [1172]. Polyester film laminates with strong adhesion, useful for electrical circuit boards and flat cables, are prepared by coating a polyester film with a plastisol containing 2EH *p*-hydroxybenzoate blocked TDI isocyanurate [1173]. A phenolic resin-paper laminate coated with an epoxy resin, polyurethane and blocked IPDI shows good adhesion to metals and plastics for support materials for printed circuits [1174]. An adhesive of poly(vinyl butyral), epoxy resin, MF resin, and oxime blocked isocyanate was applied on copper foil and hot pressed on a prepreg laminate. Peel strength and solder resistance were excellent [1175]. An adhesive consisting of epoxy resin, MF resin, poly(vinyl acetal), blocked isocyanate, and blocked catalyst is used to laminate copper foil to phenolic resin paper prepreg [1176]. Kraft paper impregnated with a polyester polyol and phenol blocked TDI is laminated with an adhesive coated copper foil to give a laminate with good impact resistance [1177]. Adhesives for bonding copper foil to prepreg that use two different blocked isocyanates with different curing temperatures with a polyester polyol [1178]. The low temperature one with a curing temperature of 100°C or less, reacts to pre-cure the adhesive on copper foil before laminating. The second phenol blocked TDI is activated during the cure when the foil is being press laminated at 170°C with a phenolic resin impregnated paper. A flexible overcoat of semiconductor chips is based on MEKO blocked IPDI trimer and an acrylic polyol [1179].

A copper clad laminate with a resist coat that has been imaged and developed is E-coated with an acrylic resin having CL blocked TDI HEMA adduct and DMAE methacrylate as comonomers, the exposed copper areas are coated [1180]. After partially curing by heating 30 min at 130°C, the panel is immersed in an aqueous solution of ethanolamine, which removes the photoresist, then the panel is immersed in an

etching bath leaving a pattern of copper covered with the E-coat. Next a solder mask resist is applied, irradiated, and developed, then the exposed part of the E-coat is removed with 1,1,1-trichloroethylene. Finally the panel is baked for 20 min at 150°C, curing the E-coat adhesive layer between the remaining copper and solder mask. A similar system uses a blocked TDI polyisocyanate reacted with sarcosine and neutralized with lactic acid with a hydroxy-functional cationic acrylic resin [1181]. In another patent, MEKO blocked TDI/TMP prepolymer is used with an anionic water-reducible acrylic resin [1182].

A photoimageable, alkali-developable solder mask is formulated with CL blocked IPDI, THEIC triacrylate, pentaerythritol tetraacrylate, a novolak epoxy resin, and a polyester terminated with phthalic anhydride [1183]. A UV curable, thermosetting photoresist coating is formulated with epoxy acrylate resin, polyacrylate monomers, and CL blocked IPDI [1184].

A waterborne electron beam cure imageable coating for flexible circuit boards is formulated with a hydroxy- and carboxylic acid-functional resin, a photopolymerizable compound, and a blocked HDI isocyanurate [1185]. A radiation curing photoresist is formulated with hydroxy-functional polyester, a photopolymerizable compound, and a blocked isocyanate [1186].

Back anti-reflective coatings (BARC) for chips are formulated with copolymers with both absorbing groups and blocked isocyanate groups for cross-linking [1187]. An anti-reflective coating is formulated with a 2-acetoacetoxyethyl methacrylate/9-anthrilmethyl methacrylate copolymer and MEKO blocked 2-isocyanatoethyl methacrylate/methyl methacrylate copolymer [1188].

A potting compound made from a blocked isocyanate/BPA-based polyurethane and a hydroxy-terminated polybutadiene showed good heat resistance and adhesion [1189]. Thermal shock resistant semiconductor potting compounds with good adhesion and low internal stress in the cured state are made with a phenol blocked isocyanate-terminated polybutadiene, an epoxy resin, an epoxy-functional silicone, and a hardener [1190]. A potting compound is made from a phenoxy resin derived from 4-4'-(1-methylheptylidene) bisphenol, BPA epoxy resin, a novolak phenolic resin, and an MEKO blocked [1191].

Photosensitive resist coatings are made from a carboxylic acid-functional acrylic resin, ethylenic monomers, a photoinitiator, and a blocked isocyanurate [1192] or MEKO blocked HDI isocyanurate, which gives high resolution resist images [1193]. DMA has been used to monitor reactions of blocked isocyanates in circuit boards [1194]. Photosensitive film overlays for printed circuit boards are made from an acrylic resin, an acrylated epoxy resin, a photoinitiator, and a blocked isocyanate [1195]. CL blocked IPDI is used as a supplementary cross-linker in a photoimageable layer in a printed circuit board [1196].

An alkali-developable photosolder resist is patented incorporating the phenol blocked TDI adduct with HEA

and an acrylated novolak epoxy resin partially reacted with tetrahydrophthalic acid to a carboxylic acid-functional derivative and a photoinitiator [1197]. An alkali-developable solder resist for printed circuit boards is made from TMP triacrylate, the diacrylate obtained by reacting BPA epoxy resin, and a methacrylic acid, HEA, methyl acrylate, methyl methacrylate copolymer, MEKO blocked HDI isocyanurate, and a photosensitizer [1198]. An interlayer electrical insulator for semiconductor devices is made from pyromellitic dianhydride and phenol blocked *p*-phenylene diisocyanate [1199].

Partially hydrolyzed ethylene/vinyl acetate polymer and CL blocked HDI are used for insulating sheaths on cables and cords [1200]. Electrical insulators for high voltage connectors are made from polyols and blocked isocyanates [1201]. Electrical insulators for wire joints are made by applying a compound of hydroxy-terminated polybutadiene and nonylphenol blocked TDI to the inside of a heat-shrinkable tube, placing the tube around a wire junction and heating to shrink the tube and cure the resin [1202].

A coating for flexible circuits is based on hydroxy-terminated polybutadiene and MEKO blocked TDI/TMP prepolymer and hydroxy-terminated polybutadiene [1203].

Resin bonded magnets for electrical motors are molded from particles obtained by spraying magnetic particles with a composition consisting of methyl alcohol blocked TDI/TMP prepolymer, poly(vinyl butyral), 2-methoxyethyl alcohol blocked TDI/TMP prepolymer with a polyether and polysulfone and then drying the particles [1204].

10.3. Magnetic coating applications

Magnetic tapes are almost exclusively coated PET film. A urethane surface treated pigment is used in manufacturing PET film for video tape [1205] or magnetic tapes [1206]. An aqueous medium for surface treating SiO₂ is made from phenol blocked HDI biuret/1,6-hexanediol/maleic anhydride resin and a polyester made with sodium dimethyl ester of 5-sulfoisophthalate as a comonomer. The treated pigment is dispersed in PET, which is extruded and biaxially drawn to make a film.

For many years blocked isocyanates have been used as cross-linkers for binders for magnetic recording materials. The binders in a two package coating for magnetic media is made with one package containing a propyleneoxidizediamine and the second package having an MEKO blocked ethoxylated glycerol-TDI resin and an MEKO blocked polyester polyurethane made with MDI [1207]. A primer is formulated with *p*-chlorophenol blocked TDI/TMP prepolymer and a hydroxy-functional polyester (the topcoat contains the magnetic iron oxide) is said to have superior peel strength [1208].

Magnetic coatings for aluminum disks are made with an epoxy resin and MEKO blocked TDI-TMP prepolymer as a binder [1209]. A magnetic oxide coating for metal disks is formulated with an MEKO blocked TDI/HDI isocyanate and a BPA epoxy resin a hydroxy-functional polyester

[1210]. Another such coating is formulated with a combination of hydroxy-functional polyester, high HMMM resin, a BPA epoxy, and an MEKO blocked polyisocyanate [1211]. A waterborne coating for magnetic disks includes an emulsion of a phenol blocked TDI and an aqueous dispersion of a thermosettable acrylic resin [1212].

A lubricating coating for magnetic disks is made with *t*-butyl alcohol blocked TDI polytetrafluoroethylene ether diol [1213].

11. Applications in photographic film and electrophotography

Several patents have been issued covering use of blocked isocyanates in various aspects of the properties of photographic film. Anti-static coatings for photographic film containing an electroconductive latex having a blocked isocyanate group have been patented [1214]. Superior post-processing stability is reported by adding sodium bisulfite blocked isocyanates to one or more gelatin layers [1215]. Similar products reduce residual color after processing [1216], show good running stability [1217], can have improved mechanical strength and scratch resistance [1218], quick drying after developing and roller mark resistance [1219], and high sensitivity, good drying properties and developability, low fog, and improved storage stability [1220]. Rapid developing films with high sensitivity and contrast are obtained when sodium bisulfite blocked HDI/polyether polyols is added to the silver halide coating [1221]. Hydrazine derivatives with bisulfite blocked isocyanates and coreactants reduce contrast reduction during aging [1222]. Imidazole blocked isocyanates added to the gelatin emulsion layer are said to give good storage stability and quick drying speed [1223]. The hardenability of gelatin is improved by use of sulfite blocked isocyanates [1224] or 2-ethylimidazole blocked HDI [1225]. Blocked isocyanate containing coatings on the face and back of photographic film improve the dryability and dimensional stability after processing [1226]. In another patent, matte coatings with blocked isocyanates for face and back sides that show good transporting properties are disclosed [1227]. A primer layer formulated with a blocked isocyanate and a carboxylic acid-function vinylidene polymer improves adhesion between the polyester support and the emulsion layer [1228].

Several patents deal with use of blocked isocyanates as cross-linking agents for binders for electrophotographic compositions. An isononylphenol blocked TDI/TMP prepolymer and an epoxy-phenoxy resin are used as the binder for a cadmium sulfide pigmented electrophotographic photoconductor layer [1229]. The photoconductive layer is formulated with isononylphenol blocked TDI/TMP prepolymer, an epoxy-silane resin, an acrylic resin, and cadmium sulfide [1230]. The photoconductive layer is formulated with a metal-free phthalocyanine, a fluoroethylene copolymer, and CL blocked HDI [1231]. The

binder of a photoconductive layer is an MEKO blocked HDI/propoxylated triol adduct [1232], or an isononylphenol blocked TDI/TMP prepolymer [1233]. A blend of a blocked isocyanate, thermoplastic acrylic polymer, and an epoxy-modified siloxane, which cross-links by reaction of the isocyanate with hydroxyl groups on the epoxy-silane [1234], or with a silicone-modified polyol resin and a blocked isocyanate have also been used [1235]. A cadmium sulfide dispersion in an carboxylic acid-functional acrylic resin with a blocked isocyanate is coated on an aluminum drum [1236]. MEKO blocked HDI with poly(vinyl butyral) [1237] or a polyester polyol [1238] is used in making coatings for an electrophotographic photoreceptor.

The charge generating layer consists of titanyl phthalocyanine pigment, ethyl acetoacetate blocked HDI biuret, and a polyol [1239]. The charge generator layer consists of phthalocyanine, a novolak phenolic resin, a phenoxy resin, and MEKO blocked HDI [1240].

The binder for an electrophotographic toner is formulated with dodecenylsuccinic acid, ethoxylated BPA, a CL blocked IPDI polyisocyanurate, and a carboxylic acid-functional polyester; another toner uses a polyester and IPDI uretdione [1241].

12. Printing and copying applications

Blocked isocyanates are proposed as components of the electrophotographic developer used in manufacturing metal lithographic plates [1242]. Methyl alcohol blocked HDI/tetraethylene glycol and DMPA prepolymer with a diazo resin is used to make litho plates [1243]. 2-Methylimidazole blocked HDI is used with an isobutylene/maleic acid copolymer that is coated on the substrate and developed with an argon laser to make a lithographic plate [1244]. Lithographic plates can be made by coating a plate with acetoacetate blocked HDI biuret-containing polymer then exposing the blank to a laser beam and developing with ethyl alcohol to make the exposed areas ink receptive [1245]. A primer for use in making lithographic plates uses an isononylphenol blocked TDI prepolymer as a cross-linker for an epoxy, carboxylic acid-functional acrylic primer [1246]. Another primer formulated with a urethane resin, blocked isocyanate, a urea resin, TiO₂, and a novolak phenolic resin has been patented for use on polypropylene film used to make plates [1247]. A lithographic plate is made by coating aluminized polyester film with an isobutylene/maleic anhydride copolymer and 2-methylimidazole blocked HDI making a thermal recording sheet that is exposed in a thermal facsimile device and developed with ethyl alcohol [1248]. Lithographic plates are proposed in which guanidine is blocked with phenyl isocyanate as a protected reactant with an epoxy resin to form a heat-sensitive transfer film [1249]. Toners for making plates are disclosed using CL blocked partially trimerized IPDI as a cross-linker for epoxy resins that have been modified with an amine [1250].

Printing inks for nylon film made with an adipic acid/1,4-butane diol/IPDI/isophorone diamine copolymer and a DEM blocked isocyanate withstand sterilization without change [1251]. Screen printing inks that give a crackled pattern on a rigid substrate such as glass are formulated with MEKO blocked HDI isocyanurate and a polyol; the crackled appearance results from an uneven initial drying followed by full curing [1252]. Lifetime of electroluminescent prints is extended by addition of a CL blocked IPDI adduct to the inks [1253].

Toners for copying machines have been patented based on a hydroxy-functional acrylic resin and blocked isocyanates mixed with an iron powder carrier [1254]. A compound from suspension polymerization of CL blocked MDI, a polyester, carbon black, and hexamethylene diamine was spray dried and mixed with a carrier to prepare a thermally fixed toner [1255]. Particles of a polyester resin, carbon black, charge-controlling agent, and carnauba wax dispersion were mixed with silica and CL blocked IPDI and a ferrite pigment to make a toner [1256]. Coated cloth for printing washable labels is prepared using blocked TDI and a polyurethane as binder for a clay coating [1257]. A laminate film of a microporous base film and a white polyester film is coated with a dispersion of a polyester polyol, a blocked isocyanate resin, and benzoguanamine–melamine copolymer particles to make a paper substitute with good printability [1258]. A polyester fiber paper is coated with dimethylformamide solution of a polyurethane resin, a blocked isocyanate, and silica as a receptor layer for ink jet recording [1259]. A plastic film is coated with a blocked isocyanate cross-linked coating to make an ink jet recording material support [1260].

In a diazo photofixing thermal recording system, 2-methylimidazole blocked HDI is included in a coating on poly(vinyl alcohol) film, which is overcoated with a layer containing a diazonium salt. After photoexposure, the film is heated and the blocked isocyanate releases the amine to develop the diazo compound, the released isocyanate reacts with the poly(vinyl alcohol) [1261]. A thermal recording material consists of a support that is successively laminated with a thermal color former layer containing a colorless electron donor dye, an electron acceptor developer which forms a color by reaction with the donor when heated, an adhesive, and a ketoxime blocked isocyanate [1262]. A thermal recording paper is prepared by coating paper with an aqueous solution containing isoamyl gallate blocked phenyl isocyanate, ferric diphenylphosphate and *N,N'*-diphenylbenzamidine [1263]. Blocked isocyanate color developers such as benzyl 4-hydroxybenzoate blocked 3,4-dichlorophenyl isocyanate are used with dye precursors in thermal recording materials [1264]. A thermal recording material is made with a sodium bisulfite blocked aromatic isocyanate and an aromatic imino compound as coloring components applied in a water-soluble urethane resin [1265].

Several patents have been issued covering various approaches for making thermal transfer recording and printing

materials. The reverse side of a PET thermal transfer film is coated with an aqueous solution of a urethane/polysiloxane prepolymer with sodium bisulfite blocked isocyanate terminal groups to give a non-sticking coating that facilitates use in thermal printers [1266]. Similar back-coated films are prepared with MEKO blocked MDI/polyurethane, an amino-modified silicone oil, and a fluorinated surfactant [1267]. PET film was coated with an MEKO blocked MDI/amine/hydroxy-modified siloxane mixture to serve as a base for a thermal transfer printing sheet [1268]. Heat-sensitive recording paper is coated with a phenol blocked TDI/TMP prepolymer gives prints with good storage stability [1269].

A color sheet for thermal transfer made with a pigment dispersed in polyester resins is used with an image receptor prepared using a blocked isocyanate [1270]. Transfer printing of steel plates primed with PVC and topcoated with a polyester is done with a paper–polypropylene transfer sheet with a hydroxy-terminated polyester and a blocked isocyanate, which is printed with a vinyl ink [1271]. Another thermal transfer recording method uses a transfer sheet containing a dye that reacts with a blocked isocyanate and a receptor sheet containing blocked HDI isocyanurate and a polyester resin. The transferred dye is fixed on the receptor sheet to form stable dye images that do not retransfer [1272]. Sublimation thermal transfer is done with a dye-receiving resin on a sheet that contains a blocked isocyanate to cross-link the dye after it sublimes [1273].

MEKO blocked MDI (or wax encapsulated aromatic isocyanate particles) and a heat developable dye are incorporated in a butadiene/vinyltoluene copolymer coating. It is applied to a PVC film to obtain a clear coating which forms a bright red color when pressed with a hot iron [1274]. MEKO blocked dichlorophenyl isocyanate and a heat developable dye in a vinyltoluene/butadiene copolymer coating gives a heat-activated film [1275].

13. Miscellaneous

Several miscellaneous applications of blocked isocyanates have been patented.

Rheology modifying cross-linked microparticles for water-based coatings are prepared from aqueous dispersions of amine salts of hydroxy- and carboxylic acid-functional polyesters and DEM blocked IPDI–TMP prepolymer [521]. Gel particles made by reacting *n*-propyl alcohol blocked TDI adduct of hydroxypropyl methacrylate and DMAE with peroxide initiator and then dispersing in acidic water are used to improve edge coverage in E-coat primers [390].

Silica fillers surface treated with HDI followed by overcoating with methyl alcohol blocked HDI in polycarbonate plastics give molded plastics with improved mechanical properties [1046]. An aqueous medium for surface treating SiO₂ is made from phenol blocked HDI biuret/1,6-hexanediol/maleic anhydride resin and a polyester

made with sodium dimethyl ester of 5-sulfoisophthalate as a comonomer [1205]. A treatment for pigments to give stable aqueous dispersion is based on an acrylic resin made with TMI as a comonomer partially reacting the isocyanate groups with polyethylene glycol and benzoic hydrazide, with the remaining isocyanate groups blocked with aminoethyl alcohol [1276].

The effects of variations in cross-link density and composition of the acrylic polymer on dimensional stability and mechanical properties of wood impregnated with blocked isocyanate and hydroxy-functional acrylic resin have been studied [1277]. Several patents cover various blocked isocyanate wood impregnating systems designed to improve durability and dimensional stability of wood: a blocked isocyanate alone in acetone [1278], BPA epoxy resin and a blocked isocyanate in acetone [1279], a hydroxy-functional acrylic resin and a blocked isocyanate in acetone [1280], and a water-dispersible blocked isocyanate and a solution of polyethylene glycol [1281]. Also a blocked isocyanate in water is used to soak wood that then shows good compatibility with fluoropolymer treating compounds [1282]. Wood blocks have been modified by grafting fluoro compounds on the cellulose by treating with MEKO blocked MDI that had been reacted with 2-perfluorohexylethyl alcohol [1283].

A water-thinned binder for particle board based on a sodium bisulfite blocked isocyanate-terminated polyether polyol/HDI/PUD has been patented [1284]. Use of MEKO blocked MDI to replace part of the melamine/urea-formaldehyde resin in the binder for particle board reduces formaldehyde emissions [1285]. A binder for chip board is made with an emulsion of the sodium salt of the product obtained by reacting maleic anhydride with a hydroxy-functional urethane prepolymer prepared by reacting TDI uretdione with TMP [1286]. Wood chips are treated with the emulsion then cured by hot pressing, during cure the uretdione groups cross-link with lignocellulose in the wood. An imidazole blocked isocyanate-terminated polyether polyol is used as a binder for wood powder in making composite moldings [1287]. Isononylphenol blocked TDI prepolymer is used with cellulosic fibers to make laminates comparable in properties to phenolic laminates [1288]. Fiberboard shims were prepared from a refined pulp stock, a phenolic resin, and a blocked isocyanate [1289].

Photochromic plastic eye glass lenses are made using 1,2,4-triazole or CL blocked hydroxy-functional isocyanate-terminated polyurethanes with hydroxy- and mercapto-functional coreactants [1290].

A flexible hardening agent for epoxy resins is synthesized by reacting half nonylphenol blocked TDI (or IPDI) with the MEK ketimine of ethanolamine, the resultant product is then reacted with polyoxypropylene diamine. After hydrolysis of the ketimine group the product is a polyether-urea-urethane-amine useful as a hardener [1291].

MEKO blocked TDI prepolymer with polytetramethylene glycol is used with BPA epoxy resins in formulating a binder for abrasive wheels [1292]. Several patents cover

use of blocked isocyanates as cross-linkers for sand foundry casting molds. Aqueous dispersion of salts of carboxylic acid-functional acrylic resin and phenol blocked TDI/TMP prepolymer mixed with sand gave good foundry molds [1293]. Isononylphenol blocked TDI/TMP prepolymer and a resole phenolic resin made from BPA and formaldehyde is used as a binder for casting molds for aluminum [1294]. A similar binder using *t*-butyl alcohol as blocking agent is disclosed [1295]. An imidazole blocked TDI-terminated polyurethane from a TMP polyether polyol is another binder [1296]. Alcohol blocked isocyanates prepared by reacting alkyl carbamates with HMMM resin have been recommended for sand core binding [1297]. Glycol blocked isocyanates prepared by reacting hydroxypropyl carbamate with HMMM (see Addendum, Section 3.2); they can be used with starch as binders for sand cores. It is suggested that these blocked isocyanates can also undergo self-condensation as well as reacting with the starch [1298].

m-Methoxyphenol blocked TDI-terminated polyether-polyol added to cement mortar mix improves the elastic and waterproofing characteristics of the mortar [1299]. Similarly, use of MEKO blocked isocyanate-terminated polyether polyols in cement compositions has been patented [1300]. An aqueous dispersion of a relatively high molecular weight polyether diol partially reacted with TDI and blocked with imidazole has been patented for use as a binder for grouts. The dispersion gels in 40 min at 20°C [6]. Coatings for concrete forming boards with good mortar release properties are formulated with a blocked isocyanate and a polyphenol adduct of an alkylene oxide [1301].

A non-ionic surfactant terminated with a bisulfite blocked isocyanate is made by reacting polyethoxylated nonylphenol with HDI and then blocking with NaHSO₃ [10]. A uretdione-functional thixotropic agent is prepared by the reaction of TDI uretdione with a maleic acid polyester diol, a polyether diol and a polyether triol [822].

TMI can be blocked with a variety of additives (such as anti-oxidants, HALS, cure retarders, etc.) to give monomers that can be copolymerized into synthetic rubbers (and presumably any other polymer made by free radical addition polymerization) [1153]. For example, phenolic anti-oxidants reacted with TMI, then copolymerized with styrene and butadiene reduce oxygen pick up of the rubber to a greater extent than a control rubber.

Aqueous dispersions of encapsulated particles of a water-dispersible MDI partial adduct of a monobutyl ether of a polyether polyol surface treated with ethylenediamine have been used as binders for fiber glass mats [1302]. Aqueous dispersions of a monobutyl ether of polyether polyol adduct of MDI is blocked with MEKO and then trimerized to give a binder for fiber glass [47].

A 20% aqueous solution of imidazole blocked TDI-terminated polyether polyol gels in a moderate time for use as a soil stabilizer [1303]. Railway track ballast is treated by mixing heated ballast and molten asphalt and CL blocked MDI hydroxy-terminated polybutadiene prepolymer [1304].

MEKO blocked HDI, a polyol, and polyurethane are used to form ceramic moldings that when fired become porous due to combustion of the binder [1305].

A waterborne adhesive for making flocked galvanized steel sheets is made with an aqueous polyurethane and a self-emulsifying blocked isocyanate [1306].

Blocked isocyanates such as *p*-nitrophenol or salicylate ester blocked TDI have been investigated as cross-linking agents for solid rocket propellants [1307]. Pentachlorophenol blocked IEM copolymers [1308] have particularly been recommended as cross-linkers for propellants. 2,4-Di-*t*-butylphenol blocked TDI has been investigated as a cross-linker for hydroxy-terminated polybutadiene. (See Section 2.5 in Addendum for discussion of catalysis of the reaction [1309].)

Reverse osmosis membranes are made by treating a cellulose acetate membrane with a PUD having two blocked isocyanate groups and one quaternary ammonium salt group [1310]. One stage of a multistage membrane is treated with a blocked isocyanate hydroxylpropyltrimethylammonium chloride adduct and a copolymer of methacrylic acid [1311]. Selective semipermeable membranes were made using sodium bisulfite blocked HDI and poly(ethylene imine) [1312] or MEKO blocked IEM hydroxylpropyltrimethylammonium chloride adduct [1313].

Back reflecting laminates with superior reflecting power and outdoor durability are made with polyurethane from MEKO blocked H₁₂MDI-terminated urethane from a polycaprolactone triol and THEIC. Before curing the polyurethane was imbedded with glass microspheres and then coated with a poly(vinyl butyral)/MF topcoat. The composite was then heat cured [1314]. A coating for use in making embedded lens retroreflective sheeting is made with a vehicle prepared by reacting a polyester polyol with excess H₁₂MDI, blocking the remaining isocyanate groups with MEKO, then partially reacting with THEIC. The balance of the cross-linking is carried out after application of the coating [1315]. Durable pavement marking tape is made by screen printing a rubber sheet with a blend of polyester polyols and MEKO blocked HDI polyisocyanurate, then spraying with ceramic anti-skid particles and glass microspheres [1316].

Optical fiber sheathing has been made using alkylphenol blocked IPDI and hydrogenated, hydroxy-terminated polybutadiene [1317]. Blocked isocyanates have been patented for use in bonding an indicator dye to an optical fiber microsensor [1318].

Air fresheners for which a gel is made in an aqueous solution of Cl₂O with 2-methylimidazole and *n*-butyl alcohol blocked HDI-terminated polyether triol have been patented [1319]. Gels containing perfumes have been patented using an imidazole blocked TDI/polyether diol and water [1320]. In another patent, similar hydrogels are used with perfumes and fertilizers, gelation occurs in about 40 min after the aqueous dispersion is made [6].

Polyurethane sponges are made with a sodium bisulfite blocked isocyanate-terminated PUD and anhydrous sodium sulfate, compression molding, curing and then extracting the salt [1321].

Various blocked isocyanate prepolymers have been patented for different techniques of immobilizing cells and enzymes [1322].

2K compounds for making dental impressions have been patented using 2-methylimidazole blocked TDI polyether polyol adduct combined with a compound containing polyglycerol [1323] and polyglycerol with poly(ethylene imine) [1324].

K pastes of 2-methylimidazole blocked TDI/polyether polyol adduct and a ZnO aqueous dispersion [1325] or polyester fabric tapes impregnated with a blocked isocyanate polyether polyol [1326] are patented for use as surgical casts and braces. The surfaces of catheters are coated with a blocked isocyanate waterborne coating [1327].

Methylimidazole blocked aromatic polyisocyanate prepolymers with a polyetherpolyol are used as gelling agents to treat waste waters [1328].

Addendum to Paper A

2.1.2. Discussion of techniques

Evidence that a 200+ MEK double rub test does not indicate full cure (or even give the same rank order of time to reach 200+ double rubs as the time to reach full cure) is given in [143] by comparison of MEK rub test results with the measurement of cross-link density by DMA analysis. FT-IR has been used to study the curing behavior of a series of blocked TDI cross-linkers [1329]. FTIR, DSC, and simultaneous thermal analysis and quadruple mass spectrometry system (STA/QMS) have been used to study deblocking of blocked isocyanates [1330].

2.2. Mechanisms and kinetics

The reactions of a reactive diluent (PHEA) with both a phenol and a hydroxyl group (the 2,2-dimethyloctanoic acid ester of the 2,3-dihydroxypropyl ester of 4-hydroxybenzoic acid) with HDI and HDI isocyanurate have been investigated [1331]. With DBTDL catalyst at room temperature, the aliphatic hydroxyl group reacts with isocyanates faster than the phenolic hydroxyl group. With DABCO or Ph₃P, the relative reactivity is reversed. The differences in reactivity are great enough to permit isolation of the two products of a monoreaction with both the alcoholic hydroxyl and with the aromatic hydroxyl (Fig. 20). The two products can be considered as an alcohol blocked isocyanate and a phenol blocked isocyanate, respectively. When a solution of the phenol substituted product with DBTDL in acetonitrile was refluxed for 12 h, it underwent transcarbamoylation to

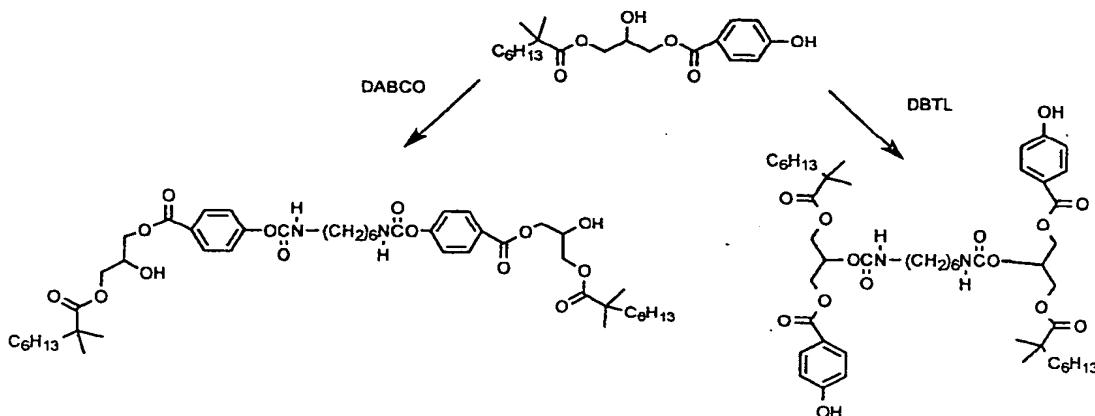


Fig. 20. Reaction product of PHEA with HDI with DBTDL catalyst and DABCO catalyst, respectively.

the aliphatic urethane product. The alcohol blocked product did not undergo transcarbamoylation with isopropyl alcohol blocked HDI under the same conditions. When used in coatings with a mole ratio of at least 1:1 NCO:total OH, both types of OH react.

Introduction of an electron withdrawing group in the alpha position of an oxime group is reported to lower deblocking temperature [469]. Oximes of alkyl esters of pyruvic acid blocked isocyanates have lower deblocking temperatures than MEKO or DMP and do not give yellowing when overbaked. Coatings cured with these oximes have good acid resistance. The esters are said to be non-toxic.

In a study of pyrazoles as blocking agents, a comparison of the rate of deblocking of a series of phenol and pyrazole blocking agents for MDI, as determined by weight loss as a function of temperature by TGA [813]. It was found that under these conditions the rate of deblocking varied directly with the boiling points of the free blocking agent (Fig. 21), it should be noted that gel times with a diamine do not follow the same trend.

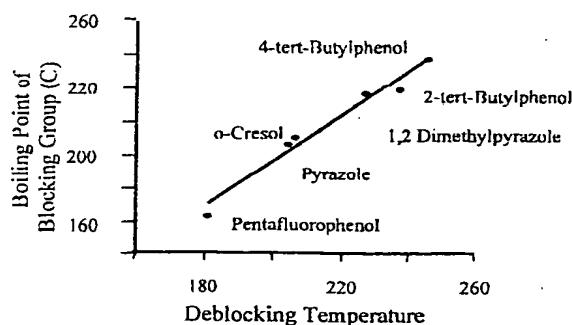


Fig. 21. Boiling points versus deblocking temperatures (determined by TGA) for a series of phenol and pyrazole blocked MDI compounds.

2.3. Effect of isocyanate structure

MEKO blocked isocyanates with oxadiazinetrione rings (see Fig. 15) are made by reacting HDI with CO₂ in the presence of tri-*n*-butylphosphine catalyst followed by reaction with triethylene glycol and blocking the remaining isocyanates with MEKO [731].

Isocyanates useful in formulating scratch and chemical resistant plastic coatings (see Section 5.4.1) are prepared by partially reacting a polyisocyanate with the product of reacting a 3-trialkoxysilylpropylamine with a dialkyl maleate and then reacting the alkoxyisilyl group with hydroxyl groups on the surface of an inorganic pigment [547].

IR and TGA are used to study unblocking of a series of diisocyanates with various blocking agents. The lowest temperature deblocking was reported to be with MEKO blocked TDI [1332].

2.5. Catalysis

In addition to the information in Paper A, see Section 4.5 for discussion of catalysis of the reactions of blocked isocyanates in waterborne coatings as well as Section 5.3.3 for discussion of catalysis of isocyanate reactions in cationic E-coats.

It has been proposed that in catalysis of reactions of blocked isocyanates with polyester and acrylic polyols, tin catalyst first complexes or coordinates with an ester group of the polyol [1333]. The complex is considered to be the active form of the catalyst. It functions by insertion between the blocking agent and isocyanate. The proposed mechanism does not characterize the next step, which may be either elimination-addition or addition-elimination. In line with this proposal, tin catalysts were said not to be very effective with polyether polyols or hydroxy-functional polybutadiene. Thus, the structure of the polyol, catalyst, and blocked isocyanate can all influence the course of the reaction. In

Table 1

Effect of catalyst concentration on MEK resistance of films of hydroxy-functional acrylic resin with benzyl alcohol blocked TTI and tetra-n-butyl-1,3-diacetoxydianoxane ($\text{Sn} = 39.5\%$) baked at 140°C for 30 min

Level of catalyst (Sn content, h^{-1})	MEK rubs
0.10	30
0.20	130
0.40	105
1.20	55

a comparison of a group of tin catalysts for the reaction of MEKO blocked isocyanates with an acrylic polyol, it was reported that the gel time at 130°C was shortest with dibutyltin butoxyethyl alcoholate [1333]. Slightly shorter gel times were reported with two proprietary tin catalysts.

A study of catalysis of benzyl alcohol blocked TTI has shown that, at least in some cases, there is an optimum tin concentration. Higher concentrations led to less catalytic effect as determined by number of MEK double rubs at temperatures lower than required to achieve 200 double rub resistance with films of a hydroxy-functional acrylic resin with benzyl alcohol blocked TTI baked for 30 min at 140°C (Table 1) [143].

A series of tin catalysts were compared at 0.2 h^{-1} of tin for their effectiveness in catalyzing the reaction of benzyl alcohol blocked TTI with two polyols. The temperature required to obtain films with 200+ MEK double rub resistance was determined with a hydroxy-functional polyester and a hydroxy-functional acrylic resin when baked 20 and 30 min, respectively (Table 2).

Seshadri et al. [1333] also found that, as in this work, blocked isocyanate-acrylic polyol systems cure faster with dialkyltin diacid catalysts while blocked isocyanate-polyester polyol systems cure faster with monoalkyltin triacid catalysts. However, Higginbottom et al. [143] report that with other polyester polyols, this reversal does not occur. The authors say that the effect of terminal groups of polyesters needs further study.

A series of catalysts was tested for the reaction of 2,4-di-*t*-butylphenol blocked TDI with hydroxy-terminated

Table 3

Catalysis of the cure reaction of 2,4-di-*t*-butylphenol blocked TDI with HTPB at 125°C

Catalyst ($1.8 \times 10^{-4} \text{ M}$)	Gel time (min)
None	315
DECHA	270
Tributylamine	285
Tribenzylamine	315
DBTDA	90
DBTDL	135
Stannous-2-ethylhexanoate	270

Table 4

Synergistic effect of amine and tin catalysts for the reaction of 2,4-di-*t*-butylphenol blocked TDI with HTPB at 125°C (concentration of amine and tin compound at $1.8 \times 10^{-4} \text{ M}$)

Amine	Tin compound	Gel time (min)
DECHA	DBTDA	30
Tributylamine	DBTDA	45
Tribenzylamine	DBTDA	70
DECHA	DBTDL	45
Tributylamine	DBTDL	60
Tribenzylamine	DBTDL	80
DECHA	Stannous-2-ethylhexanoate	75
Tributylamine	Stannous-2-ethylhexanoate	90
Tribenzylamine	Stannous-2-ethylhexanoate	120

polybutadiene (HTPB) [1309]. Table 3 gives the gel times obtained. Organotin compounds were the most effective with the less hindered DBTDA being somewhat more active than DBTDL. Diethylcyclohexylamine (DECHA) was somewhat more effective than tributylamine. However, tribenzylamine did not catalyze the reaction, presumably because of inaccessibility of the electron pair on the N.

A synergistic effect of combining amines and tin compounds was found (Table 4). Note that although tribenzylamine did not act as a catalyst alone, it did reduce the gel time of tin-catalyzed compounds although to a lesser extent than the other amines.

It is reported that dibutyl tin maleate and fumarate permit lower temperature curing (110 – 120°C) than DBTDL with

Table 2

Temperature ($^\circ\text{C}$) required to reach 200+ MEK double rub resistance as a function of catalyst (all at 0.20 h^{-1} of tin) of films of benzyl alcohol blocked with a hydroxy-functional polyester resin (films baked 20 min) and a hydroxy-functional acrylic resin (films baked 30 min)

Catalyst	Hydroxy-functional polyester	Hydroxy-functional acrylic
Tetra- <i>n</i> -butyl-1,3-diacetoxy-distannoxane	191	165
Butyltin tris(2-ethylhexanoate)	163	>177
Di- <i>n</i> -octyltin maleate polymer	191	140
Dibutyltin maleate polymer	191	149
Dibutyltin dilaurate	191	—
Dibutyltin diacetate	>150	140
Monobutyltin experimental catalyst, Fascat PE 1032	156	
Dibutyltin experimental resin, Fascat PE 1023		140
Hydrated monobutyltin oxide	163	>177
None	—	>200

MEKO blocked HDI isocyanurate and hydroxy-functional coreactants [545]. Poly(vinyl butyral), cresol blocked MDI, and DMAE gives faster cure and higher heat resistance than the same coating containing DBTDL instead of DMAE [1334].

MEKO blocked H₁₂MDI/TMP polytetramethylene glycol prepolymer with a polypropyleneoxide triamine is catalyzed with methyltriethylammonium octanoate or *N*-8-nethyl-1,8,diazabicyclo[5.4.0]-7-undecene octanoate [575].

Tetrabutyl titanate is used as a catalyst in a polyester-polyamide blocked isocyanate wire coating [671]. Bismuth neododecenoate catalyst is reported to give better package stability as compared with DBTDL and other catalysts while giving good cure response [273].

Dimethyltin iodonium and tetraphenylantimony iodonium salts have been recommended as catalysts for the reaction of an epoxy resin and phenol blocked MDI to give an oxazolidone-derived polymer [993]. The aldimine from butyraldehyde and aniline has been used as a catalyst in several patents, see, e.g. [636].

In the reaction of TACT with epoxy- and carboxy-functional resins is complicated by salt formation with the DMAP catalyst. Thus, the first reaction is addition of the carboxylic acid to the epoxy that frees the DMAP to catalyze the reaction of the TACT with other epoxy groups [507].

3.1. Phenols, pyridinols, thiophenols, and mercaptopyridines

α -Methylbenzylphenol has been patented as a blocking agent in sealants [882]. Hydrocarbon resins bearing phenolic hydroxyl groups are used to block polyisocyanates; the products have the advantage that there is no volatile blocking group (see Section 5.7 for an example of their usefulness) [755,1013].

3.2. Alcohols, other hydroxy-functional agents, and mercaptans

Benzyl alcohol [142,143,653], phenoxyethyl alcohol [1046], and methyl hydroxyisobutyrate [138] have been recommended as a blocking agents. Monoethers of resorcinol and glycols, such as 2-(2-hydroxyethoxy)phenol, are used in formulating low temperature cure E-coats [304]. 4-(Hydroxymethyl)-2,2-dimethyl-1,2-dioxalane is patented as a blocking agent [1335].

Alcohol blocked isocyanates derived from reacting HMMM and its oligomers with alkyl carbamates have been patented; they can be used to cross-link hydroxy-functional acrylic or polyester resins using tetrabutyldiacetoxy stannoxtane as catalyst [721]. Similar compounds [1297] and glycol blocked isocyanates made by reacting 2-hydroxyalkylcarbamates with HMMM have been suggested in binders for foundry sand cores [1298]. The reaction is not carried to completion, so that some

methoxymethyl groups remain on the melamine N, these groups also cross-link hydroxyl groups. Similarly, glycol monoether carbamates can be used to make blocked isocyanates for cross-linking hydroxy-functional [387] and acetoacetoxy-functional [495] acrylic resins. Acrylic monomers made by reacting IPDI, HEMA, and hydroxypropyl carbamate have been used as comonomers in making acrylic resins and latexes [83]. Alcohol blocked isocyanates on triazines that also have acrylic double bond functionality are prepared by reacting HMMM with a combination of an alkyl carbamate, such as methyl carbamate, and a compound with an acrylic double bond, such as acrylic acid, to form bis(carbamylmethyl)-bis(2-aryloyloxyethoxy)methylmelamine [821]. Such a compound is used in formulating adhesives along with an acrylate- and hydroxy-functional polyurethane and an azo free radical initiator, so that there are two cross-linking reactions occurring during cure. Alkoxy carbonylmelamines such as 2,4,6,-tributoxycarbonyl amino-1,3,5-triazine are made by reacting melamine with a dialkyl carbonate and catalyst [1336]. They can be used as cross-linkers for hydroxy- or amino-functional coreactants.

3.4. Amides, cyclic amides, and imides

CL blocked methylene diisocyanate has been prepared by reacting caprolactam-1-carboxamide with formaldehyde [118]. The blocked isocyanate has been suggested for use in powder coatings. CL blocked HDI has been synthesized without using an isocyanate by reacting carbonyl bis(caprolactam) with 1,6-hexanediamine [1337].

3.5. Imidazoles, amidines, and related compounds

Low temperature curing (100°C for 30 min) coatings are formulated with *N,N'*-diphenylformamidine blocked trimerized HDI prepolymer with 1,3-butanediol [720].

3.7. Amines

The MIBK ketimine of methylaminopropylamine has been patented as a blocking agent for TDI in E-coats [357].

3.9. Other blocking agents

A process for preparing hydroxamic acid esters for use as blocking agents has been patented [1338]. It is reported that the formyl ester of HEMA can be used as a blocking agent; the blocked isocyanate monomer can be used to make acrylic resins that do not release a blocking agent from the film during curing [1339].

Tris(succinimido)-1,3,5-triazine or its prepolymer with TMP with a hydroxy-functional polyester polyol cures in 20 min at 150°C [146]. As can be seen from the structure this is not a conventional imide blocked isocyanate, rather it is a cyclic acyl urea and has the advantage that there are no

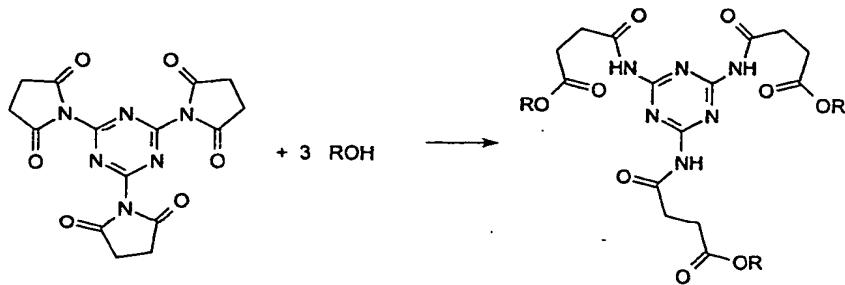


Fig. 22. 2,4,6-Tris(succinimido)-1,3,5-triazine and its presumed reaction path with a hydroxy group.

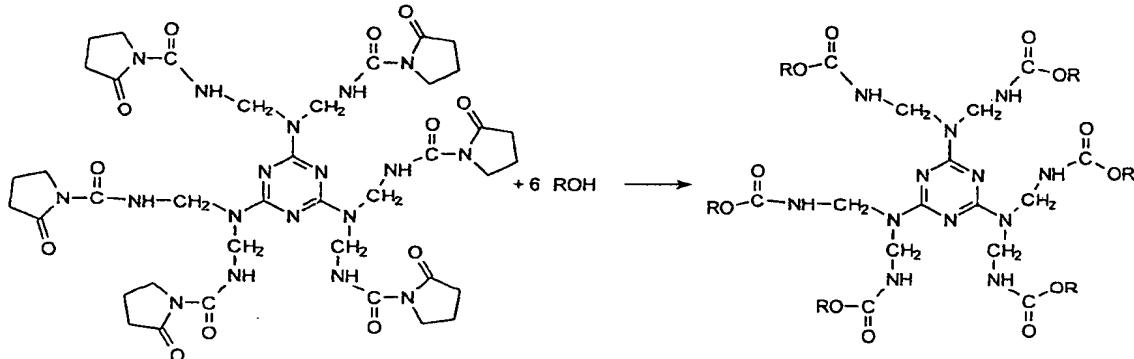


Fig. 23. Pyrrolidone urea adduct of HMMM and its reaction with a hydroxy-functional compound.

volatile byproducts. Presumably, it reacts with a hydroxyl group by ring opening as shown in Fig. 22.

Blocked isocyanates derived from reacting HMMM resin with a variety of amide ureas and oxime carbamates have been patented [119]. For example, caprolactam urea, pyrrolidone urea, MEKO carbamate, and the urea derived from reacting *N*-propyl carbamate with maleimido urea give cross-linkers that are blocked isocyanates. Fig. 23 shows the structure of the pyrrolidone urea adduct and its reaction with a hydroxy-functional resin. The cross-linking reactions are catalyzed by tetrabutyldiacetoxy stannoxane.

3.10. Uretdiones

With most catalysts, when one attempts to make HDI uretdione as significant portion of the isocyanate is converted to isocyanurate. However, using tris(dimethylamino)phosphine with an alcohol or glycol such as tetraethylene glycol as a "co-catalyst" HDI uretdione free of isocyanurate can be prepared [1340].

3.12. Comparisons of different blocking agents

The effect of varying blocking agents for TTI and some comparisons with CL blocked oligomeric IPDI and IPDI dimer has been reported (however, note that the IPDI com-

ound is difunctional compared to TTI that is trifunctional [143] (Table 5). No direct comparison with the other available carbamate cross-linker, TACT, is given, but it is reported that TACT (with pTSA catalyst) cross-links a hydroxy-functional acrylic resin in 20 min at 120°C, presumably reflecting the accelerating effect of the triazine ring [501].

DMA studies showed that cross-link density with the trifunctional benzyl alcohol blocked TTI was significantly higher than with difunctional CL blocked IPDI oligomer at the same curing schedule.

Table 5

Comparison of onset temperature (°C) of cross-linking (based on MEK double rub resistance >160) of TTI blocked with various blocking agents and CL blocked oligomeric IPDI and an IPDI dimer derivative with a hydroxy-functional acrylic resin with TK-1 (tetra-*n*-butyl-1,3-diacetoxy-distannoxane, 0.2 h⁻¹ Sn) or Fascat PE 1023 (dibutyltin experimental resin, 0.4 h⁻¹ Sn) catalyst

Blocking agent	TK-1	PE-1023
DMP	95	135
Phenol	110	177
MEKO	120	163
Benzyl alcohol	135	>200
Ethyl alcohol/butyl alcohol (90/10)	145	135
CL	158	163
<i>t</i> -Butyl alcohol	177	>200
CL blocked IPDI oligomer (0.1 h ⁻¹ DBTDL)	>177	

Table 6

Onset temperatures (°C) of deblocking of blocked isocyanates with and without polyol and cross-linking of a polyol with and without 1% DBTDL catalyst

Blocking agent	Onset T of weight loss of blocked isocyanate by TGA		Onset T of cross-linking by DMA	
	With polyol	Without polyol	With catalyst	Without catalyst
CL	177	234	163	175
MEKO	157	220	137	156
DMP	167	220	112	158
1,2,4-Triazole	150	200	121	147
Diisopropyl amine	140	220	115	136
Diethylamine			144	173
Imidazole			98	123
DEM				104

A comparison of the temperature of the onset of deblocking or a series of blocked isocyanates as determined by TGA and of onset of cross-linking as determined by DMA of a series of blocked aliphatic isocyanates with a polyol coreactant with and without 1% DBTDL catalyst has been published [1341] (Table 6).

Errata in Paper A

We have found some errors in Paper A: page 157, Fig. 24, the structures for XDI and H₆XDI should have

the substituents in the 1,3 positions instead of 1,4. In [4], the authors should be D. Katsamberis and S.P. Pappas. In [115], the inventors should be F.W.C. Lee and K.S. Baron.

Acknowledgements

The authors wish to acknowledge the extensive helpful comments and suggestions of Reinhard Halpaap, James Rosenthaler, and Clifford Schoff who reviewed various parts of the paper.

Appendix A. Acronyms

Acronym	Trivial name	IUPAC name
BPA	Bisphenol A	2,2-(Bis-4-hydroxyphenyl)propane
CL	CL	2-Oxohexamethyleneimine
DBTDL	Dibutyltin dilaurate	Dibutylbis[(1-oxododecyl)oxy] stannate
DEM	Diethyl malonate	Diethyl ester propanedioic acid
DETA	Diethylenetriamine	<i>N</i> -(2-aminoethyl)-1,2-ethanediamine
DMA	Dynamic mechanical analysis	
DMAE	<i>N,N</i> -dimethylaminoethyl alcohol	2-(Dimethylamino)-ethanol
DMP	3,5-Dimethylpyrazole	3,5-Dimethyl-1 <i>H</i> -pyrazole
DMPA	2,2-Dimethylolpropionic acid	2-Bis(hydroxymethyl)propanoic acid
DSC	Differential scanning calorimetry	
2EH	2-Ethylhexyl alcohol	2-Ethylhexan-1-ol
H ₁₂ MDI ^a	Hydrogenated MDI	Bis(4-isocyanatocyclohexyl)methane
H ₆ XDI	Hydrogenated xylylene diisocyanate	1,3-(Isocyanatomethyl)cyclohexane
HDI ^b	Hexamethylene diisocyanate	1,6-Diisocyanatohexane
HMMM	Hexamethoxymethylmelamine	<i>N,N,N',N'',N''</i> -hexakis(methoxymethyl)-1,3,5-triazine-2,4,6-triamine
IEM	2-Isocyanatoethyl methacrylate	2-Isocyanatoethyl 2-methyl-2-propenoate
IPDA	Isophoronediamine	1-Amino-3-aminomethyl-3,5,5-trimethylcyclohexane
IPDI	Isophorone diisocyanate	1-Isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane
MDI	4,4'-Diphenylmethane diisocyanate	Bis(4-isocyanatophenyl)methane
MEK	Methyl ethyl ketone	Butan-2-one
MEKO	Methyl ethyl ketone oxime	Butan-2-one oxime
MF	Melamine-formaldehyde resin	
MIBK	Methyl isobutyl ketone	4-Methylpentan-2-one

Appendix A. (Continued)

Acronym	Trivial name	IUPAC name
NMP	<i>N</i> -methylpyrrolidone	1-Methyl-2-pyrrolidinone
PUD	Aqueous polyurethane dispersion	
TACT	Tris(alkoxycarbonylamino)triazine	
TDI	2,4-Toluene diisocyanate	2,4-Diisocyanato-1-methylbenzene
TEA	Triethylamine	<i>N,N</i> -diethyl-ethaneamine
TEPA	Tetraethylenetetramine	<i>N</i> -(2-aminoethyl)- <i>N'</i> -[2-[2-(aminoethyl)amino]ethyl]-1,2-ethanediamine
THEIC	Tris(2-hydroxyethyl)isocyanurate	1,3,5-Tris(2-hydroxyethyl)-1,3,5-triazine-2,4,6(1 <i>H</i> ,3 <i>H</i> ,5 <i>H</i>)-trione
TMI	<i>m</i> -Isopropenyl- α,α -dimethylbenzyl isocyanate	1-(Isocyanato-1-methylethyl)-3-(1-methyl-1-ethenyl)benzene
TMP	Trimethylolpropane	2-Ethyl-2(hydroxymethyl)-1,3-propanediol
TMXDI	<i>m</i> -Tetramethylxylylene diisocyanate	1,3-Bis(1-isocyanato-1-methylethyl)-benzene
TTI, NTI, TIN	Nonane triisocyanate	4-Isocyanatomethyl-1,8-diisocyanatoctane
XDI	Xylylene diisocyanate	1,3-(Isocyanatomethyl)benzene

^a Some authors use HMDI, potentially confusing with HDI which is sometimes called HMDI. Others use rMDI, "r" standing for reduced.

^b Some authors use HMDI, potentially confusing with H₁₂MDI which is sometimes called HMDI.

Appendix B. Commercial blocked isocyanates

Trade names and compositions of blocked isocyanates found in the literature. Some of the identifications are based on statements in patents and are not necessarily correct.¹

Trade name	Supplier	Isocyanate	Blocking agent
Additol VXL 81	Hoechst		Ethyl acetoacetate
Adiprene BL 16	Uniroyal	TDI polyether elastomer	MEKO
Adiprene L-167	Uniroyal	TDI polytetramethyleneether glycol	MEKO
Alcure 4470	McWhorter	IPDI	1,2,4-Triazole
Baybond-116	Bayer	HDI prepolymer	MEKO
Baytec VP-PU 50 EL 05	Bayer	Polymeric HDI	Dispersion of surface-treated particles
Baytec VP-PU 50 EL 07	Bayer	Polymeric HDI	Dispersion of surface-treated particles
Bayhydrol BL 116	Bayer	HDI isocyanurate (water dispersible)	MEKO
Bayhydrol VP LS 2016	Bayer	(Water dispersible)	MEKO
Burnock B3-867	Dai Nippon Ink	HDI	?
Burnock D7-887-60	Dai Nippon Ink	HDI isocyanurate	MEKO
Burnock D 500	Dai Nippon Ink	TDI	?
Burnock D 550	Dai Nippon Ink	HDI isocyanurate	MEKO
Burnock DB 980K	Dai Nippon Ink	HDI	?
Coronate 2501	Nippon Polyurethane	HDI polyisocyanurate	?
Coronate 2503	Nippon Polyurethane	MDI	Phenolic
Coronate 2507	Nippon Polyurethane	HDI isocyanurate	MEKO
Coronate 2512	Nippon Polyurethane	MDI	?
Coronate 2513	Nippon Polyurethane	HDI isocyanurate	DEM

¹ In many cases, the only information available just gave the base diisocyanate monomer and did not disclose whether the isocyanate was a monomer or in a polymeric form (i.e. biuret, isocyanurate, or prepolymer) or left out exact description of the blocking agent. In other cases, no information was available on one or the other. There were also some for which we were unable to identify the supplier. We did not list many other products where there was no compositional information. The list also includes some that are no longer commercially available.

Appendix B (*Continued*)

Trade name	Supplier	Isocyanate	Blocking agent
Coronate 2515	Nippon Polyurethane	HDI isocyanurate	CL
Coronate 2517	Nippon Polyurethane	HDI	?
Coronate 2527	Nippon Polyurethane	HDI	?
Coronate 2529	Nippon Polyurethane	HDI	?
Coronate AP	Nippon Polyurethane	TDI/TMP prepolymer	Phenolic
Coronate CT	Nippon Polyurethane	TDI isocyanurate	Phenolic
Crelan TP LS 2668	Bayer	IPDI/COOH-functionality prepolymer	CL
Crelan UI	Bayer	IPDI	CL
Crelan VP LS 2147	Bayer	IPDI uretdione prepolymer	None
Crelan VP LS 2181/1	Bayer	Diisocyanate that also has a COOH	CL
Desmocap 11	Bayer	TDI polyether polyol prepolymer	Isononylphenol
Desmocap 12	Bayer	TDI prepolymer	Phenolic
Desmodur 44 M	Bayer	IPDI	CL
Desmodur 4265	Bayer	IPDI polyisocyanurate	MEKO
Desmodur AP-Stabil	Bayer	TDI/TMP prepolymer	Phenolic
Desmodur BL 100	Bayer	TDI polyester prepolymer	CL
Desmodur BL 1100	Bayer	TDI polyester prepolymer	CL
Desmodur BL 1265	Bayer	TDI prepolymer	MEKO
Desmodur BL 3175	Bayer	HDI polyisocyanurate	MEKO
Desmodur BL 3272	Bayer	HDI polyisocyanurate	CL
Desmodur BL 3370	Bayer	HDI polyisocyanurate	Diisopropylamine and DEM
Desmodur BL 3475	Bayer	HDI/IPDI polyisocyanurate	DEM and ethyl acetoacetate
Desmodur BL 4165	Bayer	IPDI polyisocyanurate	MEKO
Desmodur BL 4265	Bayer	IPDI polyisocyanurate	MEKO
Desmodur CT-Stabil	Bayer	TDI isocyanurate	Phenolic
Desmodur KL-5-2371	Bayer	IPDI	Ethyl acetoacetate
Desmodur LS 2759	Bayer	HDI polyisocyanurate	Acetylacetone
Desmodur TPLS 2957	Bayer		CL
Desmodur TT	Bayer	TDI uretdione	None
Desmodur VP LS 2111	Bayer	H ₁₂ MDI	MEKO
Desmodur VP LS 2114	Bayer	IPDI polyisocyanurate	Diisopropylamine/1,2,4-triazole
Desmodur VP LS 2117	Bayer	H ₁₂ MDI	MEKO
Desmodur VP LS 2252	Bayer	IPDI polyisocyanurate	DMP
Desmodur VP LS 2253	Bayer	HDI polyisocyanurate	DMP
Desmodur VP LS 2257	Bayer	HDI polyisocyanurate	MEKO
Desmodur VP LS 2307	Bayer	H ₁₂ MDI	DEM
Desmodur XP 7018E	Bayer	MDI prepolymer	MEKO
Desmodur XP 7098E	Bayer	IPDI (?)	?
Duranate 17B 60PX	Asahi	HDI biuret	MEKO
Duranate E402 B80T	Asahi	HDI isocyanurate elastic adduct	MEKO
Duranate MF B60X	Asahi	HDI isocyanurate	MEKO
Duranate MF K60X	Asahi	HDI isocyanurate	DEM
Duranate TPA-B80E	Asahi	HDI	?
Duranate TPA B80X	Asahi	HDI isocyanurate	MEKO
Duranate WF-B60X	Asahi	HDI	?
Duranate WF-K60X	Asahi	HDI	?
Elastron BN 69	Daiichi Kogyo Seiyaku	MDI	MEKO
Elastron C 9	Daiichi Kogyo Seiyaku	?	Bisulfite
Elastron C 37	Daiichi Kogyo Seiyaku	PUD	Bisulfite
Elastron E 37	Daiichi Kogyo Seiyaku	HDI-based PUD	Bisulfite
Luxunate HC 1170	Lyondell	IPDI polyisocyanurate	DMP

Appendix B (Continued)

Trade name	Supplier	Isocyanate	Blocking agent
Luxunate HC 2170	Lyondell	HDI biuret	DMP
Luxunate IC 1170	Lyondell	IPDI isocyanurate	MEKO
Millionate MS 50	Yotsuya Urethane	MDI	Cresol
Mondur HCB	Bayer	TDI/HDI isocyanate/isocyanurate	MEKO
Mondur L	Bayer	TDI/HDI isocyanate/isocyanurate	MEKO
Mondur S	Bayer	TDI prepolymer	Phenol
Mondur SH	Bayer	TDI isocyanurate	<i>m</i> -Cresol
Powderlink BI 10	Cytec	TMXDI	CL
Prominate XC 910	?	TDI/TMP adduct	MEKO
Rhodocoat XD 2 D	Rhodia	HDI isocyanurate	3-Hydroxybenzoate
Rucote NI 2	ARCO	IPDI (partially trimerized)	CL
S 202	?	Aromatic	Nonylphenol
Su 125 Z	?	Aromatic	Phenol
Sumidur BL 3175	Sumitomo-Bayer	HDI isocyanurate	MEKO
Synthrapret BAP	Bayer	HDI propylene glycol prepolymer	Bisulfite
TAUT	Cytec	2,4,6-Triisocyanatotriazine	Methyl/butyl alcohols
Takenate 140 N	Takeda	IPDI	MEKO
Takenate 160 N	Takeda	HDI	MEKO
Takenate B 83D	Takeda	TDI	MEKO
Takenate B 815 N	Takeda	H ₁₂ MDI	MEKO
Takenate B 820 NSL	Takeda	H ₁₂ MDI	MEKO
Takenate B 842 N	Takeda	H ₆ XDI	?
Takenate B 845 N	Takeda	H ₆ XDI	MEKO
Takenate B 846 N	Takeda	H ₆ XDI	MEKO
Takenate B 870 N	Takeda	IPDI	MEKO
Takenate B 874 N	Takeda	IPDI	MEKO
Takenate B 882 N	Takeda	HDI	MEKO
Takenate B 883 NS	Takeda	TMXDI	MEKO
Takenate PW 2400	Takeda	MDI	CL
Takenate WB 700	Takeda	TDI (waterborne)	MEKO
Takenate WB 720	Takeda	HDI (waterborne)	MEKO
Takenate WB 730	Takeda	XDI (waterborne)	MEKO
Takenate WB 820	Takeda	HDI (waterborne)	CL
TANtBzC	Solutia	TTI	Benzyl alcohol
Tolonate D2	Rhodia	HDI isocyanurate	MEKO
Tolonate XTHT	Rhodia	HDI polyisocyanurate	?
Trixene 199-76 X	Baxenden		DMP ?
Trixene BI 7673	Baxenden	TDI	?
Trixene BI 7770	Baxenden	TDI	?
Trixene BI 7772	Baxenden	TDI	?
Trixene BI 7773	Baxenden	TDI	?
Trixene BI 7779	Baxenden	TDI	?
Trixene BI 7981	Baxenden	HDI isocyanurate	?
Trixene BI 7982	Baxenden	HDI isocyanurate	?
Trixene BI 7983	Baxenden	HDI isocyanurate	?
Trixene BI 7984	Baxenden	HDI isocyanurate	?
Trixene BI 7960	Baxenden	HDI biuret	?
Trixene BI 7961	Baxenden	HDI biuret	?
Trixene BI 7962	Baxenden	HDI biuret	?
Trixene BI 7950	Baxenden	IPDI	?
Trixene BI 7951	Baxenden	IPDI isocyanurate	?
Trixene BI 7952	Baxenden	IPDI isocyanurate	?
Trixene BI 7982	Baxenden	HDI isocyanurate	DMP

Appendix B (Continued)

Trade name	Supplier	Isocyanate	Blocking agent
Trixene BI 7985	Baxenden	HDI isocyanurate (water dispersible)	?
Trixene BI 7986	Baxenden	HDI isocyanurate (emulsion)	DMP
Vestanate B1192	Cleanova	HDI (partially trimerized)	MEKO (half-blocked)
Vestanate B 1358	Cleanova	IPDI isocyanurate	MEKO
Vestanate B 1370	Cleanova	IPDI adduct	MEKO
Vestanate B 1530	Cleanova	IPDI (partially trimerized)	CL
Vestanate BF 1300	Cleanova	IPDI uretdione	?
Vestanate BF 1310	Cleanova	IPDI uretdione	?
Vestanate BF 1540	Cleanova	IPDI uretdione	?
Vestanate EPB 2094	Cleanova	IPDI/TMP prepolymer	CL
Vesticoat EP-DS-2779	Cleanova	Isocyanurate with water-reducible polyurethane-acrylic	MEKO
U-Lock Q 9061	?	Polybutadiene-polyisocyanate	Phenolic

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